# MANUFACTURE OF ALUMINIUM

PATTISON, ALUMINIUM]

Werner, Pfleiderer's Universal Kneading and Mixing Machine

THE MANUFACTURE
OF ALUMINIUM

WITH

FULL NOTES ON ALUMINIUM ALLOYS,
THE ANALYSIS AND EXAMINATION OF
ALUMINIUM WORKS MATERIALS, AND THE
MANUFACTURE OF CARBON ELECTRODES

BY

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FRONTISPIECE AND 18 ILLUSTRATIONS

783

N 181

CONTENTS.

PAGE

PREFACE.

A FEW years ago, whilst in charge of the Chemical Laboratory of The Aluminium Corporation, Limited, Wallsend-on-Tyne, I had exceptional opportunities for studying the process there in force, and consequently collected a good deal of information on the subject.

It naturally occurred to me that, as information on the manufacture of aluminium was of a very scattered and meagre nature, an account of its manufacture from the early days of its production up to the present time, also the applications of the metal, would be most interesting to the general reader and those connected with the industry.

Methods of analysis for aluminium metal, aluminium alloys, and the materials used in the course of the manufacture of aluminium, that would give a sufficient degree of accuracy and be completed within a reasonable time, would be invaluable to those called upon to examine them. With these objects in view the present small volume has been compiled.

Although the writer feels his inability to treat the subject as comprehensively as he would like, at the same time he earnestly hopes that the reader will find this small work both interesting and useful.

If the reader finds it so, then the object of this book will be accomplished.

In conclusion, I acknowledge my indebtedness to the Admiralty for permission to publish, and shall always be glad to receive hints from readers as to possible improvements in its contents.

<div align="right">J..T. PATTISON.</div>

PORTSMOUTH, *June* 1918

ALUMINIUM.

CHAPTER I.

HISTORICAL SURVEY OF PROCESSES.

THE seed from which the electrolytic method for obtaining metals may be said to have begun to give fruit was the discovery of Humphry Davy, for he was one of the most successful of the early workers.

Having settled the vexed question as to the acid formation at the anode, previously observed by Nicholson and Carlisle, Humphry Davy in 1807 succeeded in decomposing the alkali metals by means of the electric current. As may be imagined, this discovery caused some excitement and interest, as at that time the alkali hydrates were believed to be elementary bodies—an erroneous idea. Davy, following up his discoveries of sodium and potassium, in 1808 produced the carbide of sodium by the aid of the electric arc, and he also separated the metals calcium, strontium, barium, and magnesium from the alkaline earths by use of the method first applied by Berzelius, in which mercury was employed as negative electrode and formed an amalgam with the metal separated.

Davy also succeeded in decomposing alumina. In his experiment, a layer of alumina, previously moistened with water and kneaded together, was placed on a sheet of platinum, which in turn was connected to the positive pole of a voltaic pile, comprising a thousand pairs of plates.

Into this mass, from the top, was introduced an iron wire connected with the negative pole of the above pile. The iron wire was soon raised to a white heat, and melted where in contact with the alumina The metallic mass, when cold, was found to be more white and brittle than iron, and on dissolving in acids a solution was obtained from which alumina could be separated.

Faraday, a former pupil and assistant of Davy, following up the study of electrolysis, achieved important and remarkable results.

His experimental work, carried out in the Laboratories of the Royal Institution, London, during the years 1812 to 1840, was undoubtedly instrumental in placing the science of electro-metallurgy upon a firm basis of accurately observed phenomena, without which the present - day electrolytic methods of obtaining aluminium would be unsuccessful.

The first account of the isolation of aluminium is that of the decomposition of its chloride, by means of potassium, carried out by Aerstad about 1824 to 1827. In this reaction the chlorine parts from the aluminium chloride to combine with the potassium, and thus the aluminium is set free. Wohler effected some improvements in Aerstad's process, he being the first to obtain the metal in malleable globules.

It is, however, to Deville, in 1858, and independently to Bunsen, in 1864, that we are indebted for a process which admitted of application on a manufacturing scale. He first obtained aluminium chloride thus :—Alumina mixed with powdered charcoal was made into a paste with oil, heated in a tubular retort, not unlike those sometimes used in the manufacture of coal gas, whilst a current of dry chlorine was made to pass through the vessel. Under these conditions, carbonic oxide and aluminium chloride are formed.

The volatile aluminium chloride was sublimed into a chamber lined with glazed tiles, where it condensed as a yellow translucent mass. Some of the aluminium chloride

ѵas then placed in a tube, towards the end of which a long ɪarrow tray or boat, containing pieces of sodium, were ɪnserted, and dry hydrogen passed through the apparatus.

The sodium was then gently heated, and the aluminium ᴄhloride caused to distil over it; thereby the aluminium ᴄhloride was reduced with a vivid glow. The aluminium ɪet free collected in the tray, together with the double ᴄhloride of sodium and aluminium, which was produced at ᴛhe same time. The tray was then removed, and more ᴛtrongly heated in a porcelain tube, through which a ᴄurrent of hydrogen was passing. The metal was thus ᴏbtained in globules :—

$$AlCl_3 + 3Na = 3NaCl + Al.$$
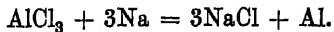
In 1859, F. W. Gerhard manufactured small amounts of ᴀluminium at a small factory at Battersea, England. From 1860 to 1874, Messrs Bell Bros., under Deville's supervision, ᴘroduced nearly two cwts. per year at their works at Washing-ᴛon, near Newcastle-upon-Tyne, England. They exhibited ᴛhe metal at the International Exhibition of 1862, quoting ᴀ price of £2 per lb. troy.

The year 1851 stands out very conspicuously, for in that ᴠear a remarkable patent was taken out by one Charles Watt, in which he describes in detail how the electric current ᴍight be employed for producing the alkali hydrates, ᴄhlorine, hypochlorites, or chlorates, from solutions of the ᴀlkali metal chlorides, and how it might be utilised for ᴛefining silver, copper, and other metals, or for separating ᴛhese from their ores.

However, it was not until 1869 that Watt's ideas received ᴀny practical trial, when Elkington erected the first electro-ᴄopper refinery at Pembrey. During the next few years, ᴳramme introduced improvements into the design of ᴅynamos which greatly improved their efficiency.

Since then, many further improvements have been made

from time to time, to keep up with the requirements of the
electro-chemical and electro-metallurgical industries.

   Coming now to the more modern methods of manufacturing
aluminium, the Cowles, Hall, and Héroult are the chief.

   The Cowles process was started in 1886 at Milton in
Staffordshire, England, and at Lockport in America in the
same year. The process, during the early days of the
industry, was thermal and not electrolytic in character,
depending upon the reduction of alumina by carbon, in the
presence of copper or iron, at a red heat, the electrical
current being employed merely as a source of heat.
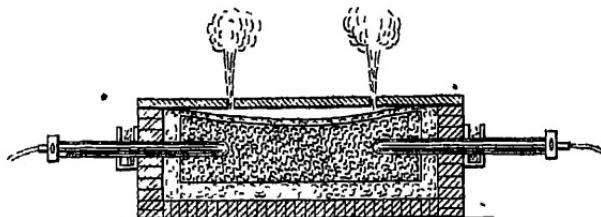
FIG. 1.

   Carbon itself is unable to effect the reduction of alumina
below a temperature of 2 100° C, but in the presence of
copper or iron reduction is practicable, since the affinity of
the two metals and disposition to form an alloy induces the
alumina to part with its oxygen more readily. The process
consisted of heating powdered corundum, a natural form of
alumina, with charcoal and iron filings in a large electric
furnace. 5 000 amperes at 60 volts were employed for heat-
ing, and one and a quarter hours were required for reducing
each charge. The yield was stated to be 1 lb. of alloy per
18 E.H.P. hours.

   When granulated copper was used instead of iron, an alloy
containing upwards of 30 per cent. aluminium was obtained.
The dynamo at the Milton works for supplying the current
was of 300 K.W. capacity, and at the date of the trial, 1888,

was the largest then built in this country. In fact, engineers from far and wide went to view it, as at that time it was considered quite a marvellous achievement.

In 1892, these two works ceased operations, owing to the rapid development of the Hall and the Héroult processes, and to the fact that pure aluminium could not be manufactured by the Cowles furnace.

The Hall method of alumina reduction, first operated
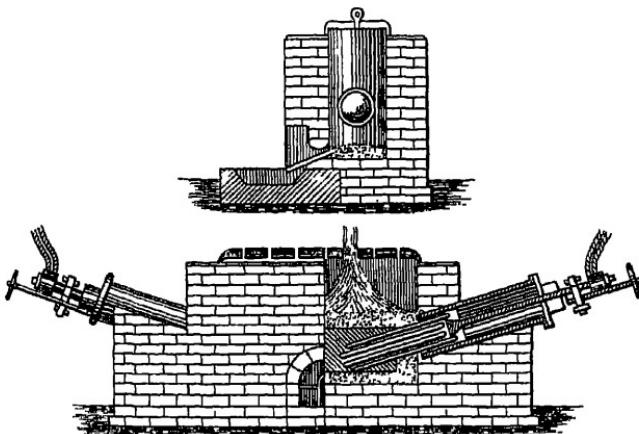
FIG 2.—Front View of Cowles Furnace for the production of Aluminium Alloys.

in America in 1888, is at present employed at three works in that country, also at Calypso, near St Michel, and St Félix in France, all of these works being operated by water power.

The process is electrolytic in character, and depends upon the use of the fused electrolyte, cryolite, together with fluorspar and alumina. The original patent specifies 169 parts of aluminium fluoride and 116 parts by weight of potassium fluoride, part of the latter being replaced by lithium fluoride to lower the melting-point of the mixture.

In the early days of the industry the mineral bauxite

was added direct to the furnace, but it was soon evident that pure aluminium could not be obtained by this procedure, hence the use of very pure refined alumina

Pure alumina used to be prepared by the ignition of ammonium alum, or by the precipitation from a solution of alum free from iron, but at present it is almost exclusively prepared from the mineral bauxite, as described in a following chapter on the preparation of pure alumina.

Cryolite is a mineral occurring in vast quantities in Greenland, and has the chemical formula $6NaF,Al_2F_6$ when pure. Artificially prepared cryolite has been found to work satisfactorily, although it is more readily decomposed by the electric current than the natural variety.

Fluorspar is a crystalline variety of calcium fluoride, and has the chemical formula CaF_2.

When these three, cryolite, fluorspar, and alumina, are melted together, the alumina dissolves in the mixture of fluorides, and if the electric current be then passed through the mixture, using carbon electrodes, the aluminium separates out in the molten state at the cathode. The alumina alone is decomposed if the current be kept below 6 volts, the cryolite and fluorspar remaining unaltered in the bath, serving merely as a solvent for the alumina. The molten aluminium, being heavier than the molten electrolyte, sinks to the bottom of the furnace, a most important thing for the success of the electrolytic process. The oxygen at the anode combines with the carbon of the anode, forming carbon dioxide, and, since a very pure form of carbon is essential for the production of pure aluminium, the carbon electrodes form an important item in the total cost of production.

Hall's patent expired in 1905.

The process worked out by M. Héroult, a French metallurgical chemist, in the years 1886 to 1888, was begun on an industrial scale at Neuhausen in Switzerland in the year

1889. Up to 1891, only copper-aluminium alloys were manu-
factured at these works. But since then owing to modifica-
tions introduced into the process, pure aluminium has been
the chief product at Neuhausen and at the other half-dozen
European works

In Héroult's original patent
specification, an iron crucible,
20 cm. depth by 14 cm. dia-
meter, lined with blocks of
carbon, the walls and base
being used as negative elec-
trodes as in Hall's process,
and the carbon anodes, 5 cm.
in diameter, suspended in the
molten bath, were described.
The current was 400 am-
peres, at from 20 to 25 volts,
the voltage being four to five
times that specified by Hall.

The electrolyte was com-
posed of fused alumina, with-
out any admixture. Molten
copper was, however, used
on the floor of the bath, so
that, as soon as the current
liberated any aluminium
from the alumina, combina-

FIG 3 —Sectional View of a modern
Electric Furnace for the produc-
tion of Aluminium.

tion took place, with the formation of aluminium bronze.

At present, however, the process is identical with that of
Hall. Indeed, these two processes are so similar that it is sur-
prising to find distinct patents and organisations for them.

The cost of alumina to produce one ton of aluminium is
about £25, and the cost of electrical energy by the Héroult
process about £12 per ton. If the aluminium is sold in bulk
at £130 per ton, the allowance for carbons, labour, deprecia-

tion, interest on capital, and profits, must be nearly £100 per ton, which admits of a good profit.

At the British Aluminium Company's Héroult Works, Foyers, in Scotland, the process is carried out in iron smelting-vessels having carbon-lined floors of a clear cross-section of about 1 500 mm. by 750 mm. (4′ 11″ × 2′ 5½″), with currents of 8 000 amperes, corresponding in round numbers to a current density of 7 000 amperes per square metre (650 amperes per square foot). The Aluminium Corporation, Ltd., use similar furnaces, being a shade larger.

The electrolyte is kept at the necessary degree of fluidity, namely, 900° C. to 950° C., about half of the electrical energy being required for this purpose, the other half performing the actual electrolytic dissociation of the alumina into metal and oxygen.   The electrical pressure required is 5 to 6 volts. The output, of course, depends on the number of amperes supplied at this pressure. Above 6 volts the cryolite decomposes Alumina is added to the furnace at regular intervals as that dissolved is decomposed. The surface of the electrolyte is kept covered with powdered coke to prevent loss of heat by radiation.

Owing to the difficulty of obtaining pure calcium fluoride, the addition of this ingredient, which had the effect of lowering the melting-point of the mixture, has in recent years been dispensed with.

As will be seen from the following table, a mixture of 95 per cent. cryolite with 5 per cent. of alumina gives the lowest melting-point ·—

Per cent. $Na_3AlF_6 + Al_2O_3 =$ melting-point, ° C.

100	+	–	=	1 000
97	+	3	=	974
96	+	4	=	960
95	+	5	=	915
94	+	6	=	960
93	+	7	=	982

In considering the theoretical output of such furnaces as those of Héroult and Hall, the following fundamental facts are necessary. Faraday's laws, expressed concisely and in modern language, state that electricity is only conveyed through electrolytes by the ions, and that equal quantities of electricity are transported with chemically equivalent quantities of the ions.

The quantity of electricity which is transported by one gram-ion of hydrogen is 96 540 coulombs, then, we know from Faraday's law that the passage of this quantity corresponds with the discharge at the electrodes of one gram-ion of every other monovalent ion, half a gram-ion of every bivalent ion, one-third of a gram-ion of every trivalent ion, and so on. Or, conversely, the liberation, or deposition, or separation of every monovalent gram-ion requires the passage of 96 540 coulombs, every bivalent gram-ion the passage of $2 \times 96\,540$ coulombs, every trivalent gram-ion the passage of $3 \times 96\,540$ coulombs, etc. Thus the gram-ions may be regarded as vehicles capable of transporting 96 540 coulombs, $2 \times 96\,540$ coulombs, $3 \times 96\,540$ coulombs, etc., according as they are mono-, bi-, or trivalent, etc.

Now suppose we wish to find out how much aluminium can be theoretically produced by a current of 1 000 amperes acting continuously for a year of, say, 300 days on a bath of fused alumina in a suitable flux, such as cryolite.

In alumina the aluminium is trivalent, hence for the separation of one gram-ion or 27·1 grammes, we must pass $3 \times 96\,540$ coulombs, or ampere-seconds. The maximum quantity of aluminium that can be produced by a current of 1 000 amperes in 300 days is therefore

$$\frac{27 \cdot 1 \times 1\,000 \times 300 \times 24 \times 60 \times 60}{3 \times 96\,540} = 2\,425 \text{ kilograms.}$$

The quantity of aluminium which is separated by the passage of 3 600 coulombs, $i.e.$ per ampere-hour, is 0·336 8 grammes.

We will now consider the electrical energy required to keep the bath in suitable state of fluidity.

As is well known, there is a definite relationship between electrical energy and other forms of energy, such as mechanical energy, heat energy, etc.

$$1 \text{ volt-coulomb} = 10^7 \text{ erg.} = 0\cdot102 \text{ kilogram-metre} = 0\cdot24 \text{ gram-calorie.}$$

Electrical energy is the product of the quantity expressed in coulombs, and of the potential expressed in volts.

A similar relationship exists between electric energy and chemical energy, but, unfortunately, at present, we know next to nothing of chemical energy, or of its factors. If, however, we measure the change in chemical energy by the heat evolved, or absorbed, during the chemical reaction, and if it is further assumed that the whole of this heat can be converted into electrical energy and made available as an electrical current, then we would simply have the relationship ·—

Electrical energy (expressed in calories) = Heat of the reaction.

The exact measure of the electrical energy in volt-coulombs is $E \times N \times 96\,540$ for an N-valent gram-molecule, or, since 1 volt-coulomb = $0\cdot24$ gram-calorie, the exact measure of the electrical energy in gram-calories is $E \times N \times 96\,540 \times 0\cdot24$. If the corresponding heat of the reaction is Q gram-calories, then the relation would be ·—

$$E \times N \times 96\,540 \times 0\cdot24 = Q,$$

or

$$E = \frac{Q}{(N \times 96\,540 \times 0\cdot24)} \cdot$$

If this relationship, usually known as Thomson's theorem, is applied to alumina, it may be shown that the E.M.F. required to decompose alumina is about $2\cdot8$ volts, which is reduced

to 2·2 volts if the oxidation of the anodes is considered as part of the reaction

The greater expenditure of electrical energy in practice results in the production of heat which maintains the bath in a molten condition. After allowing for the electrical energy required for the decomposition of the alumina, the total heat developed by the expenditure of the remaining quantity, expressed as electrical energy, may be calculated from the equation

$$H = 0.24 \ C^2Rt \text{ gram-calorie,}$$

where

H = calories,

0.24 = mechanical equivalent of heat,

C = amperes,

R = ohms,

t = time in seconds.

The temperature which is obtained in the electric furnace depends on a variety of circumstances, such as the mass of material immediately surrounding the heated conductor, its conductivity both for heat and, incidentally, for electricity, its specific heat, and the time in which the heat is developed, etc. For example, a kilowatt-hour, when transformed into heat, yields 864 000 calories, no matter whether the transformation occurs in a second or in a year. Practically, however, the effect produced would be quite different in the two cases. If the transformation took place in a second, the temperature of the resistance might rise to an enormous extent; while, if it spread over a year, there might be no appreciable rise in temperature at all, owing to the radiation or conduction away of the heat as fast as it was produced.

If it is desired to estimate the least amount of energy to be supplied by a dynamo for the decomposition of the alumina, the only satisfactory way of doing so, as far as we know at present, is to determine experimentally the decom-

position potential of the alumina, or the lowest E.M.F. required to produce a sensible current, and then to combine this with the theoretical current output calculated from Faraday's law.

In actual practice a higher E.M.F. will, of course, be required, while in general the current output will be less than the theoretical.

The ratio of the energy actually consumed to that calculated on the above basis is the nearest approach we can make to the energy efficiency of the process.

Previous to 1907, the only producer of aluminium in America was the Pittsburg Reduction Co., which controlled three plants, namely, at Niagara Falls, Massena, New York, and at Shawinegan Falls, Canada. At these works cast-iron troughs lined with carbon were used, the anodes consisting of 48 carbon rods, 15 ins. long by 3 ins. diameter, which are manufactured by the Aluminium Company for their own use. Each furnace took about 10 000 amperes at 5·5 volts, and yielded 1·75 lbs. of aluminium per horse-power day.

Several other processes for the production of aluminium by electrolysis have been tried, but were not successful, except those of Hall and Héroult, by which practically the whole of the world's output of aluminium at the present time is obtained.

One of the most striking failures to maintain its position occurred in connection with the development of the Webster and Castner process. Commenced at the Oldbury Works, Birmingham, England, by the British Aluminium Company in 1887, the process was a purely chemical one, the reduction of the aluminium compounds being effected by the action of metallic sodium upon a mixture of aluminium fluoride and aluminium chloride at a red heat. Three years later the Oldbury Works had to suspend operations by the Castner and Webster process, for the Héroult process

in Europe and the Hall process in America were producing
a very pure metal by their electrolytic methods.

The " Minet " aluminium reduction process, as far as can
be seen, appears to be essentially identical with the Hall
process, and has indeed been worked in conjunction with it
at St Michel in France.   Perhaps the simplest way of under-
standing the difference between the Héroult, the Hall, and
the Minet processes is to consider their differences to consist
in legal rights as defined by the dates of patents.

Bücherer's process is worthy of note, for there is a possi-
bility it may eventually supersede the present-day methods.
Bücherer uses aluminium sulphide in place of alumina,
dissolved in cryolite.

He claims that if the correct temperature be maintained
the sulphur could be recovered as a by-product and a
great saving of carbon obtained, as will be seen from the
following equations :—

$$(1) \qquad Al_2O_3 + 3C = Al_2 + 3CO ;$$
$$(2) \qquad 2Al_2S_3 \qquad = 4Al + 3S_2 ;$$
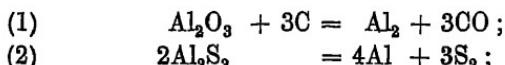
thus reducing the cost of production considerably.   If the
temperature be too low, or too high, then some carbon
disulphide is formed, the amount depending upon the con-
ditions—quantity and pressure of current, temperature,
and the rate at which the final products are removed.

$$2Al_2S_3 + 3C = 4Al + 3CS_2$$
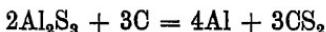
According to " Blount and Bloxam," at 3 volts, only alumin-
ium and sulphur are produced, no carbon disulphide being
formed.

CHAPTER II.

ALTHOUGH a comparatively new commercial metal, next to silicon, aluminium is one of the most abundant constituents of the earth's crust, it being computed to comprise over 8 per cent of our earth. The name aluminium is derived from alumen, a word applied by the Romans to anything of an astringent taste.

Aluminium is not found in the uncombined state, but in combination with oxygen as alumina; and in the form of silicate constituting the various clays, such as kaolin, $Al_2O_3,2SiO_2,2H_2O$, and as compound silicates in the felspar, it occurs in enormous quantities.

As alumina it occurs in nature as the precious stones amethyst, emerald, ruby, and sapphire. Interesting mention might here be made that artificial sapphires were obtained fifty years ago by Deville and Caron, but their results could not be obtained by subsequent workers. Verneril, however, by heating alumina with 1·5 per cent. magnetic oxide of iron and 0·5 per cent. titanium dioxide in the reducing part of the oxyhydrogen flame, has produced crystals which are identical in properties with the natural stone, the colour being due to the lower oxides of iron and titanium.

Aluminium, as alumina, occurs in such minerals as corundum and bauxite, the latter consisting of hydrated alumina associated with iron oxide, constituting the chief source

14

from which the metal itself is obtained.   It is also found
as cryolite, a double fluoride of aluminium and sodium,
$Al_2F_6,6NaF$, and as a hydrated phosphate in the various
forms of turquoise.   Alumina also occurs in the region of
Kraubat in Upper Styria in vast quantities as bauxite,
an impure hydrated oxide, which takes its name from the
district of Baux near Arles, in France, where it is found in
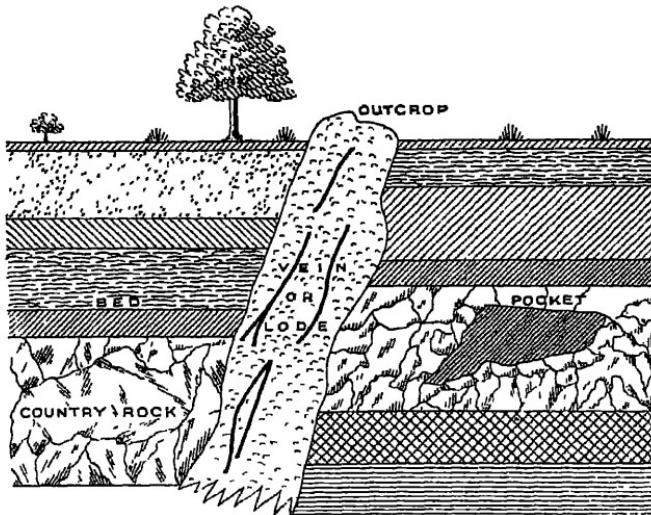

Fig. 4 —Figure showing how Bauxite occurs on the Earth's
surface

conjunction with calcareous beds.   This mineral rarely exists
in a pure state, but contains varying amounts of ferric
acid and silica, a good-class ore containing from 60 per cent.
to 75 per cent. alumina.

Many of the bauxite deposits seem to be true precipitates,
formed by the action of water upon its salts, but others
suggest a metasomatic origin, part of the alumina being
replaced by other bases.   As a type of the locality of Baux,
and several other localities in France, also in the Georgia-

Alabama districts of the United States, the bauxit
associated with limestone, in which they occur eit
masses of irregular shape or as well-defined beds [1]

The Georgia-Alabama district is one of the oldest
three main groups into which the normal fossiliferous
are divided, forming the first legible volume of the
history—the Palæozoic period—consisting of lime
underlaid by pyritous shales, and dissected by nur
highly inclined fault planes.

One of the most probable explanations is that the a
ing meteoric waters, acting on the pyrites of the shal
rise to ferric sulphate and sulphuric acid. The sul
acid, in coming into contact with alumina of the shale,
forming alum and aluminium sulphate, which are c
upwards by the ascending currents. The ascending
tions of aluminium and iron sulphates, on coming into c
with limestone, will act metasomatically upon it, wii
formation of calcium sulphate and deposits of hy
oxides of aluminium and iron.

Some of the bauxites in the Alabama district con
layers and masses of ore embedded in a residual clay
result of prolonged weathering of the limestone series.

Bauxite is also found embedded in clay at Oberhesse
Vogelsburg in Germany.

In the Puy-de-Dôme country of Central Franc
Westerwald, Vogelsburg, and the north of Ireland, b
occurs in association with basaltic rocks, and is reg
as having been formed from these igneous masses
obscure metasomatic process. The deposits of Baux
mostly as irregular masses in cretaceous limestones, it
suggested that they were laid down by the aid of m
springs. Although such an origin is extremely likel
action which was brought about by the precipitatio

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[1] Bauxite occurs plentifully in British Guiana, and is being
out on a large scale to meet the demand for war requirements.

almost certainly metasomatic, and dependent on the chemical action of the limestone.

With regard to the mineral corundum, found in India, Thibet, and China, evidently the alumina was dissolved in the original magma, at the time of its intrusion into the country rock, and that at an early stage, as the mass began to cool, it separated out, together with other rather insoluble oxides.

From laboratory experiments it has been found that alumina is soluble to some extent in molten magnesium silicate, and, if the homogeneous mass has no excess of magnesia, then all the alumina crystallises as corundum ; but, on the other hand, if there be a slight excess of magnesia over the magnesium silicate, some of the alumina will combine with it and crystallise as spinel (MgO, Al_2O_3).

Also, sedimentary aluminous rocks, under great pressure, and subjected to the heating influence of the earth's interior, or to that of some intruded igneous mass, will undergo a marked change, such as the formation of corundum.

Certain rocks, in which the contained alumina is not in excess of the silica, will under such conditions give rise to the metamorphic aluminium silicates, such as alusite, cordierite, and cyanite   But should the alumina be more than equivalent to the silica, the excess of alumina crystallises as corundum.   Hence the metamorphosis of a highly aluminous deposit results in the formation of an almost pure mass of this mineral ; and it is an interesting fact to note that the changing of bauxite into corundum has been effected in the laboratory by means of the electric furnace.

CHAPTER III.

As the electrodes come into direct contact with the reduced metal, it is of the utmost importance that the electrodes should be as free as possible from injurious mineral matter, such as silica, iron, etc. They must not be liable to crack, and must possess a high conductivity, and also have a good contact arrangement between the carbon and metal conductor. Blocks that give a good ringing sound when struck, usually show a high conductivity also. Blocks having a high specific gravity and a low porosity are not liable to crack.

The specific gravity of the different states of carbon varies thus :—

Calcined anthracite has a sp. gr. of about 1·80
Calcined oil coke   ,,   ,,   ,,   2·00
Kilned retort carbon ,,   ,,   ,,   2·05

The usual procedure for making the carbon electrodes is as follows :—

(1) The petroleum or oil coke is first calcined to remove the greater part of the volatile matter and increase the specific gravity, consequently the conductivity.

(2) The coke is then crushed until a good gristing is obtained.

(3) The ground coke is mixed with the binding material, usually pitch, or tar and oil, in a steam-jacketed mixer.

(4) The mixture is moulded.

(5) The blocks are kilned in a furnace for from four to six days, at a temperature approaching 1 000° C., after which the blocks are cooled, and brushed ready for use.

The petroleum coke is obtained in the distillation of shale oil, it being the residue, and contains about 8 per cent. of volatile hydrocarbons, together with an average of 0·2 per cent. ash.

The calciners are vertical, square brickwork constructions capable of taking a charge of two hundredweights, at the top, every two hours. A half charge is withdrawn every hour by means of rakes, the coke taking five hours to travel from the top to the bottom.

The next step, the gristing, is very important. The amount of fine dust and larger pieces of coke must be properly proportionate to obtain the block with the highest specific gravity and least porosity.

A good gristing is :—

To pass through a 100 meshes per square inch					40	parts	
,,	,,	,,	60	,,	,,	15	,,
,,	,,	,,	30	,,	,,	20	,,
,,	,,	,,	16	,,	,,	15	,,
and between 16 and 18				,,	,,	10	,,

From the grinding mills the ground oil coke is transferred by means of hoppers to the mixing machines, which are of the steam-jacketed kneading type, with reversing gear, for changing the direction of motion.

Sufficient of the binding material, usually pitch, is worked into the coke by means of the mixing machine, so that, when some of the mixture is squeezed in the hand, it just coheres together.

The binding material usually forms 20 per cent. of the whole mixture. Instead of using pitch as a binder, a mixture of 85 parts of hard pitch, with a density of 1·26, containing

about 60 per cent. of volatile matter, with 15 parts of asphalt oil of a density of 0·96, and containing not more than 1 per cent of moisture, answers much better.

The ingredients are mixed for about twenty minutes in the " mixers," by means of revolving blades, at a temperature of about 90° C.

The mass is then tipped from the " mixer " on to a platform, and immediately transferred by means of shovels to a press, where it is moulded under a pressure of one ton to the square inch by hydraulic power.

The " blocks " are usually about 10 inches square by 12 inches in height, and have rounded tops. A piece of mild steel is fixed into each block as it is being moulded, the internal end being forked, and is placed about one-third way into the block, so as to have a firmer hold. The blocks are then allowed to stand a few days to harden before they are calcined.
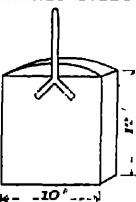

FIG 5 —Sketch of Carbon Electrode Block.

Before being calcined, some carbon blocks were coated with pitch after moulding, and then stored for about one week before firing in the tunnel furnace. These were found, owing to the denser surface, to have a longer life than those not so treated.

In the calcination, the blocks are placed on small waggons, the forked-steel contact in the carbon block covered by fireclay covers, and the whole well packed over with fine ashes. The waggons are made to fit the furnace, which is a long brick tunnel structure, capable of holding 24 waggons in a row. The furnace ends have iron doors made to slide up and down by means of counterpoises.

In introducing a fresh waggon of electrodes to be calcined, the doors are opened and the waggon pushed in by means of the hydraulic ram, which causes another waggon that has

traversed the whole length of the furnace to emerge from
the other end of the furnace.

The fuel used is producer gas, usually generated from a gas
producer of the " Mason " or " Wilson " type (fig 6).   The
flues are situated near the bottom of the furnace, about the
middle of the length of the furnace.   The temperature of the
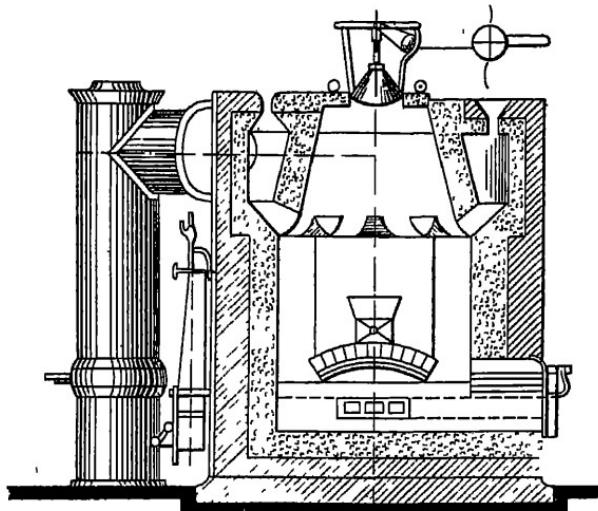
FIG   6.—Wilson Gas Producer

furnace should be from 900° C. to 1 000° C.   On cooling, the
blocks are brushed and stored for use.   A " block " lasts
about 120 hours   They contract 3 to 5 per cent on cooling.

The finished electrodes should have an electrical resistance
of about 0·001 6 ohm, be capable of conducting a current of
25 amperes per square inch of cross-section, and have an
apparent density of 1·55 to 1·70, a real density of 1·95 to
2·05, and the ash should be below 0·3 per cent

CHAPTER IV.

In the early days of aluminium production, cryolite and aluminium chloride were decomposed by treatment with metallic sodium. At the present time, alumina dissolved in cryolite is decomposed by electrolysis. It is absolutely necessary that the alumina and cryolite be pure to obtain the metal in the pure state.

Alumina used to be prepared by the ignition of ammonium alum and alum free from iron, or from the mineral "Bauxite " by fusion with sodium carbonate for about six hours in a reverberatory furnace, when carbon dioxide is evolved and sodium aluminate formed.

The aluminate was then extracted with water and filtered, a stream of carbon dioxide passed through the clear solution to precipitate the aluminium hydrate, with regeneration of sodium carbonate, the latter being recovered and used to attack a fresh quantity of bauxite. The aluminium hydrate was then washed, dried, and calcined.

At the present time, however, alumina is exclusively prepared from bauxite by " Baeyer's process," as follows :—

The crude bauxite, which chiefly consists of aluminium and iron hydrates, is ground fairly fine, kilned to destroy any organic matter, and "kiered " with a solution of caustic soda of a specific gravity of 1·45, usually under a pressure of 70 lbs. to the square inch, although some manufacturers

use less pressure. The British Aluminium Company use a pressure of about 50 lbs. to the square inch for about eight to ten hours.

The mass is then blown out by its own internal pressure into a tank and diluted to a convenient concentration, usually until the liquid has a specific-gravity of about 1·23, so as not to wear the asbestos filter presses through which it is then passed, to separate the insoluble silica, iron, and titanium hydrates, etc.

The sodium hydrate is next agitated with alumina, prepared by a previous operation for from thirty to thirty-six hours, when about 70 per cent. of the alumina present in the solution is thrown out, precipitated. The white semi-flocculent precipitate of hydrated alumina is next filtered, washed free from soda, and partially dried.

The filtrate, after concentrating to the original specific gravity, 1·45, is used to attack a fresh quantity of bauxite. The partially dried hydrate of alumina is then calcined at a temperature of 1 000° C., this high temperature being necessary to obtain the alumina in a crystalline form, which is less hydroscropic than the amorphous variety. The former variety may be stored for months or conveyed by sea without taking up an appreciable amount of moisture. The hydrate is of a pinkish tinge, which is not lost till calcined several days at a temperature of over 800° C.

Alumina appears to exist in different modifications, so far as its physical character is concerned. Thus some varieties are crystalline while others are amorphous. Some are denser than others, as shown by determinations of specific gravity, and some varieties retain moisture more persistently than others, so that, as previously stated, a very high temperature is required to ensure their perfect dehydration.

A further difference is to be observed between various forms of alumina, when the coloured light yielded by them during their phosphorescence under electric discharge in high

vacua is studied.   These colours vary from blue, blue-green, and purple to red.   Generally, a specimen of alumina which exhibits a red phosphorescence is highly crystalline, possesses a high specific gravity, and shows very little tendency to absorb moisture.   Thus a sample of alumina, dried at 100° C , having a formula $Al_2O_3,3H_2O$, i.e. 65·39 per cent. Al_2O_3 with 34·61 per cent. water, did not part with all its water at temperatures below 900° C., but after heating at 950° C. for twelve hours it lost practically all its water, and did not exhibit marked hygroscopic properties ; but on heating to 1 600° C for one hour the density increased to 3·88, gave a red phosphorescence, and no spirting occurred while it was being submitted to electrolysis.   After seven days' exposure to the atmosphere the moisture was found to be 0·33 per cent.

Red Mud.

This is the residue left after extraction of the alumina with caustic soda, for an analysis of which see " Analysis of Red Mud."   At present this is a waste by-product, but no doubt will be put to profitable uses in the near future. A few suggestions for its utilisation are .—

By the removal or conversion of the alkali present into a non-deleterious substance it could be employed as a pigment. If made porous, use could be made of it for the purification of coal-gas,such as for freeing the gas from sulphur compounds. The author found that when the red mud is mixed with 2 to 3 per cent. of sawdust, or chalk, and then kilned, a marked change in the porosity was produced, which would probably make it more suitable as an absorbent of the sulphur compounds in crude coal-gas Unfortunately, so far as the author is aware, thus treated, the red mud has not yet been tried on the large scale.

He suggests that the most profitable procedure for utilising the red mud appears to be the following :—

Say, extraction of the aluminium and titanium by fusion

with caustic soda, lixiviating and utilising the aluminate and titanate of soda as a mordant in the dyeing industry, then dissolve the oxide of iron in a suitable flux and separate the iron electrolytically.

Artificial Cryolite.

This is very little used at present, as the price is the same as the natural mineral, which occurs in an almost pure state abundantly in Greenland.

Large quantities of artificial cryolite have been prepared by just passing hydrofluoric acid gas into a solution containing sodium alum, with subsequent washing, and fusion of the resultant cryolite in an atmosphere of hydrofluoric acid gas, and then powdering for use.

The natural product is not so readily decomposed by the electric current as the artificial cryolite, hence, when the latter is used as an electrolyte, a larger quantity is required; but, on the other hand, a corresponding amount of metal is obtained, due to the decomposition of the artificial cryolite.

CHAPTER V.

THE FOUNDING OF ALUMINIUM.

ALUMINIUM metal from the electric furnace is always recast before being put upon the market. This is done in a reverberatory furnace (fig. 7), the body of which, containing the aluminium, is made of iron and arranged with an outlet for
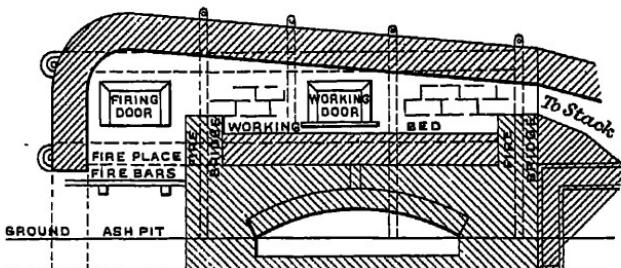

FIG. 7.—Reverberatory Furnace.

pouring the metal into ingots. The fuel is usually coal, although some of the waste heat from the tunnel furnaces used for calcining the carbon blocks might be utilised for this purpose in the future. For small castings the metal is melted in plumbago crucibles, and for large castings the melt is done in a furnace lined with iron and made to tilt over for pouring

In casting aluminium and its alloys, it is of the utmost importance that the metal should be cast at as low a temperature as possible, for, although the melting-point of aluminium

is only 625° C., it requires a large quantity of heat to melt it. Professor J. W. Richards estimates that the amount of heat in one kilogramme of aluminium is 258 calories, and the latent heat of fusion 100 calories.

The appearance when heated should only reach a dark red, as when superheated and exposed to the air nitrogen is absorbed, which is again evolved on cooling; therefore, if cooled too rapidly the nitrogen is unable to escape, causing the metal to become porous.

The skimmings from overheated metal in contact with a moist atmosphere smell strongly of ammonia, which indicates the presence of the nitride

$$2Al_3N_3 + 9H_2O = 3Al_2O_3 + 6NH_3.$$

The metal should be thoroughly stirred to allow the oxide to rise to the top where it is skimmed off. In pouring, the flow should be kept in a continuous stream, when the oxide surrounding the stream of metal will act as a syphon, preventing any further oxidation, giving clean and sound castings. A moulder will not go far wrong if he remembers that :—

Yellow brass cannot be cast at too high a temperature ; phosphor bronze cannot be cast at too dull a temperature ; gun-metal should be cast at a " nice heat " ; and anti-friction metal should never be allowed to come to a red heat ; and, of course, the latter specially refers to aluminium.

When casting aluminium, its large shrinkage, which amounts to about 2 per cent., must be allowed for, and in casting pieces with cross-section the mould should be undone and the sand carefully loosened as soon as possible, or the shrinkage will cause the casting to crack.

In drawing rods or wire the metal is annealed well at frequent intervals, otherwise its tensile strength will be greatly diminished. Casting too hot or in dry sand deadens the colour.

The fracture grain differs according to the methods of treat-

ment.   When drawn, rolled, or forged the metal shows a silky
grain.   Pure aluminium has a linear expansion of 0·000 023,
and a mean specific heat from zero to its melting-point of
0·218 5.   A cubic foot of aluminium weighs 167·1 lbs.

The method of casting affects the density slightly ; thus
aluminium of 99·7 per cent. purity,

> Sand cast   has a specific gravity of 2·69
> Chill cast   ,,   ,,   ,,   2·70
> Rolled bars   ,,   ,,   ,,   2·71
> Drawn bars   ,,   ,,   ,,   2·71

The following mechanical tests are given by Dr Carpenter
and C. A. Edwards, from which it will be seen that working,
such as rolling, drawing, or forging, considerably increases
their tensile strength.   Thus rolled bars of pure metal :—

Diameter.	Yield point Tons per square inch	Ultimate stress Tons per square inch.	Elongation. Per cent.	Reduction in area Per cent.
1¼″	4 40	6·50	35·5	79 35
⅛	6·50	7·20	30·5	81·20
(Drawn bars in the same metal).				
⅛	7 00	7 42	23 0	82·05
(Cold-drawn bars in the same metal)				
⅛	8 50	8·72	19·5	73·28

The tensile strength diminishes with rise in temperature,
as seen from the following determinations by André le
Chantelier : —

Temperature, de-
  grees Centigrade   = 15°, 100°, 150°, 200°, 250°, 300°, 400°, 450°, 400°.
Tensile strength, tons
  per square inch . =11·68, 9·5, 8 1, 6 3, 4·8, 3·6, 2 4, 1·5, 1·0.

All are agreed that the secret of success in aluminium
casting lies in the melting.   Therefore, too much care cannot
be taken to prevent overheating the metal.

CHAPTER VI.

ALLOYS OF ALUMINIUM.

ALUMINIUM unites with most of the common metals forming definite chemical compounds, which crystallise out in a matrix of practically pure aluminium, but the characters of these alloys do not recommend themselves for the purposes to which aluminium is applied Hence the metals which can be employed in the alloy are usually limited to a few which form solid solutions with aluminium. These include zinc, manganese, and magnesium. However, copper and nickel are exceptions, both metals being employed as hardening agents, though they belong to the class first mentioned.

> Zinc up to 13 per cent. increases the strength.
> Nickel, ,, 5 ,, ,,
> Copper ,, 4 ,, ,,

The further addition of one of these metals to aluminium gradually diminishes the tensile strength. Thus, according to the Alloys Research Committee, when 4 per cent. of copper is reached a decrease of ductility commences as the copper contents increase, whilst the tenacity does not correspondingly increase. The most marked increase in strength takes place in the 2 to 3 per cent. copper alloys.

One of the manganese alloys made and examined by the Alloys Research Committee, containing 2·15 per cent. copper and 1·91 per cent. manganese, showed, as sand castings, on the tensile tests, a yield point of 6·68 tons per square inch,

ultimate stress 8·10 tons per square inch, and elongati
5 per cent. ; whilst as chill castings the results showed : yie
point 7·80 tons, ultimate stress 10 tons, and elongati·
5 per cent.

The manganese alloys showed no marked superiori
over the corresponding copper-aluminium alloys, althou{
it was clearly shown that the alloys were very sensiti
to the method of casting adopted and to variations in t
casting temperature.

Several magnesium alloys have been put upon the mark
under such names as " magnalium." Although up to 10 p
cent. of magnesium has been suggested as giving good resul{
owing to the expense of such an alloy rarely more tha
2 per cent. magnesium is employed.

Magnesium aluminium alloys usually contain small amoun
of copper, nickel, and tin, while some contain silicon
quantity.

Silicon hardens aluminium, and is sometimes added up {
5 per cent. for that purpose, but more than 2 per cent rende
the alloy less malleable.

A comparatively new alloy known as " Duraluminium
has been brought out by Vickers, Son & Maxim. Th
remarkable alloy is only slightly heavier than aluminium, bι
is as strong as mild steel, can be rolled, drawn, stampec
extended, or forged at suitable temperatures, and is le{
corrosive than other high aluminium alloys under all th
usual corrosive tests.

One analysis of the alloy gave :—

Al	.	.	.	= 94·60 per cent.
Cu	.	.	.	3·90 ,,
Fe	.	.	.	0·45 ,,
Mg	.	.		0·75 ,,
Si	.	.	.	0·21 ,,
Mn	.	.	.	trace
				99·91

As an alloy made by the Alloys Research Committee approximating to the above did not show properties in accordance with those of duraluminium, it is quite possible the new metal owes its properties to its mechanical treatment. The minor constituents are those usually employed in non-ferrous foundry work as " deoxidisers," from which we may infer that special attention has been given to deoxidising the alloy thoroughly   It is also a well-known fact that when pouring these alloys a comparatively small rise in temperature will greatly reduce the strength of the casting. Certainly " duraluminium " is a wonderful example of the metallurgist's art ; but then the old saying that " there is nothing new under the sun " reminds one that ancient copper chisels have been found which are as hard as present-day steel—an art lost and not yet regained. It has also been suggested that the hardness may be due to a physical change taking place in the course of time.

Aluminium bronze (generally regarded as the discovery of Dr Percy) usually contains 90 per cent. copper and 10 per cent. aluminium, has a greater shrinkage than gun-metal, and is difficult to machine on account of its high tensile strength.

An alloy known as " Henssler's Alloy," containing copper, aluminium, and manganese, is distinctly magnetic.

Another patent alloy, " Timalium," is made by adding small quantities of manganese and zinc to aluminium whilst in the molten state. This alloy is much harder than aluminium, is easily forged, filed, drilled, and has a lower conductivity than the pure metal.

An aluminium-titanium alloy was obtained by " Wöhler " by melting together

Titanium dioxide (TiO_2) . . .	2 parts
Cryolite (Na_3AlF_6) . . .	6 ,,
Sodium and potassium chlorides ($NaCl, KCl$)	6 ,,
Aluminium (Al)	1 part

and then dissolving out the excess of aluminium with caustic soda solution. Bright steel-coloured crystals were obtained having a specific gravity of 2·7 to 3·3, containing aluminium, titanium, and a little impurity from the aluminium used.

These crystals were infusible before the blowpipe, and on heating in chlorine gas combustion took place with formation of chlorides of all the metals present. Heated in the air, they first became yellow, then steel-blue, after which oxidation ceased.

Michel also obtained an alloy the analysis of which denoted the formula Al_3Ti; and L. Levy by a similar process obtained an alloy in crystalline plates, steel-grey in colour, having a specific gravity 3·11, insoluble in water, alcohol, or ether, and conducting heat and electricity.

Messrs Brearly and Ibbotsen found the analysis of two ferro-aluminium-titanium alloys, made by smelting scrap iron and titanium ore in an electric furnace, to be :—

				No. 1.		No. 2.	
C	.	.	.	0·20	per cent.	0·32	per cent.
Si	.		.	2·89	,,	1·06	,,
Mn	.	.		0·60	,,	0·75	,,
S			.	0·014	,,	0·06	,,
P				0·064	,,	0·12	,,
Ti	.			28·00	,,	34·62	,,
Fe	.	.		67·20	,,	61·28	,,
Al	.	.	.	1 00	,,	1·48	,,

Commercial ferro-titanium contains about 50 per cent. titanium with about 3 per cent. carbon. A special quality is also made containing only 0·5 per cent. carbon, and has been suggested in general use as a deoxidiser and denitrofier in the iron and steel founding, its efficiency for the first purpose being undoubted.

The ferro-aluminium made by the Cowles process, according to Prof. Mabery, gave on analysis the following :—

	No. 1.	No. 2.	No. 3.
Fe	85·17 per cent.	85·46 per cent.	84·00 per cent.
Al	8·02 ,,	8·65 ,,	10 50 ,,
Si	2·36 ,,	2·52 ,,	2·40 ,,
C	..	..	2·50 ,,

According to the general testimony, the advantages of using the above alloy in the foundry are : the castings come out of the sand cleaner and sharper, are more free from blow-holes, work more uniformly in the lathe or planer, and are generally stronger.

Thos. Shaw of New Jersey, U.S.A., made an alloy containing 0·33 per cent. to 5 per cent. of aluminium, 0·50 per cent. to 1 per cent. of phosphorus, the remainder being copper.

A compound of phosphorus and aluminium was made by Wöhler by heating finely divided aluminium in phosphorus vapour, when combustion took place, with the formation of a dark grey metallic mass which smelt strongly of phosphuretted hydrogen in the presence of moisture. This gas was also evolved copiously when placed in water :—

$$2AlP + 3H_2O = 2PH_3 + Al_2O_3$$

The following are some of the common aluminium alloys in use :—

	Al	Cu	Nl	Zn	Pb	P.	W	Si.	Sn	Use
1	86·7	0·8	..	12·5	..	·	·	..	..	Used for light slabs and thin plates of maximum hardness and strength.
2	86·0	1·5	..	12·5	..	..	..	..	..	Bars and thick plates. War Office fuse caps.
3	84·0	3·0	..	13·0	..	·	..	·	..	The best white aluminium casting alloy, flows well, especially good in either sand or chill moulds, giving clean, sharp castings, is stronger than Nos. 9, 16, and 5. Used largely for motor fittings. Sold under the trade name of "Croml."
4	77·0	3·0	..	20·0	..	·	·	..	..	Gives a low shrinkage, good sharp castings, etc., where raised impressions have to be taken.
5	96·0	4·0	..	..	..	·	·	·	·	Strong alloy, used largely for motor and cycle castings. Castings can afterwards be recut or riveted cold. When worked, has high tensile strength.
6	98·5	·	1·5	..	..	..	··	..	·	Stamping metal.
7	95·0	·	5·0	..	..	..		..	·	" "
8	90·0	·	..	10·0	..	..		..	..	Cheap castings; give good white alloy; flows well, giving clean, sharp castings; cheaper and stronger than pure aluminium.

No.	1	2	3	4	5	6	7	8	Remarks
9	98 0	2 0							Hardened sheet.
10	76 0	4 0		20·0					For castings: low shrinkage.
11	10 0	90 0							General use; resembles gold; strong; has non-corrosive properties.
12	86·0				2·5	0 5		11 5	In making this alloy about ½ lb of phosphorus in the form of sticks is added to every 100 lbs of alloy per cent of P taken up; varied a lot.
13	98·0	2·0							In making this alloy 1 per cent of tungsten is added to the molten mass, which simply removes the dross to the surface, that is, the Al_2O_3 and suspended matter. Nearly the whole of the powder is either skimmed off again or is left in the bottom of the pot in running the alloy out. W does not alloy with Al, but with stirring 1 or 2 per cent W can be obtained in suspension
14				11·0	5·0	10 0		74 0	The phosphorus is introduced as phosphor tin. Used as an aluminium solder.
15	70 0			30 0					Cheap castings, such articles as tea or coffee stands.
16	7 5	90·5					2 0		Silicon bronze, very free from blowholes.
17	10 0	85·0	5 0	(5 per cent. tungsten used in making)					Propeller bronze
18	10 0	80 0	5 0						,, ,,
19	2·0	65 0		33 0					" Hercules Bronze " for general use.

A very interesting paper was read before the Institute of Metals, at Newcastle-upon-Tyne, on 21st September 1911, by Walter Rosenhain, B A., D.Sc., and Sidney L. Archbutt, A.I.C , on "The Thermal Properties and Microstructure of the Aluminium Zinc Alloys," to which I would refer those who are interested.

Aluminium forms an amalgam with mercury, which may readily be prepared by placing aluminium filings into a 0·5 per cent. solution of corrosive sublimate ($HgCl_2$).

The amalgam decomposes water energetically at ordinary temperatures, with the liberation of hydrogen and the formation of aluminium hydrate. Hence it is used where a neutral reducing agent is required.

The energetic reaction is due to the fact that the mercury prevents the finely divided aluminium from oxidising on the surface in the air ; for when a'uminium itself is oxidised on the surface, such surface oxide prevents the metal underneath from being attacked.

CHAPTER VII.

THE USES AND APPLICATION OF ALUMINIUM.

FROM the following figures it will readily be seen that as the metal became cheaper its application to various uses increased enormously. Thus in 1887 aluminium cost £1 per lb., or £2 240 per ton. In 1890 the world's output yielded about 40 tons, costing £1 083 per ton; whereas during 1897, 2 500 tons were produced, costing £145 per ton , from which time the output has increased enormously, until at the present time aluminium can be bought for about £130 per ton, and the estimated output of the world is over 20 000 tons.[1]

Aluminium is a white, silvery-looking metal, slightly heavier than two and a half times its bulk of water, its specific gravity being 2·65. Hence most of its applications are due to its extreme lightness, and to the fact that it does not tarnish to any extent on exposure to the atmosphere.

Annealed aluminium is exceedingly soft and ductile, and second only to gold in malleability. It can be rolled into sheets of less than six ten-thousandths of an inch in thickness, and afterwards beaten into leaf. It can also be drawn into fine thread.

The electrical conductivity of commercial aluminium is between 55 to 61 per cent. that of copper, when wires of equal sectional area are compared. But as aluminium is only a

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[1] Owing to war conditions price per ton has considerably increased.

third the weight of an equal bulk of copper, the cost of the two metals of equal carrying capacity is about the same.

Several thousands of tons of the light metal have now been employed as overhead conductors, which have been found to work very satisfactorily, although in some districts, owing to the impure nature of the atmosphere, caused by certain manufactures, the wires are very seriously corroded.

An overhead line of over twenty-two miles has been erected between the Niagara Falls and Buffalo, transmitting 15 000 horse-power. In California, the North Yuba Power Company have a transmission line sixty-three miles long in operation.

Aluminium added to steel in quantities of two to eight ounces per ton frees the iron of any small amounts of oxygen it might contain, at the same time causing the castings to have a sharp fineness. The so-called " Mitis " steel has been so treated

When over 17 per cent. of aluminium is present in steel, the alloy is found to be magnetic. If aluminium powder be mixed with granulated ferric oxide, and the charge be ignited, say, with a piece of burning magnesium wire, an intense combustion occurs, the aluminium combining with the oxygen of the ferric oxide, whilst the latter is reduced to molten metallic iron The heat evolved during the reaction is so great and intense, that both the alumina and the iron are obtained in the molten condition at a white heat.

This mixture is now obtained on the market under the name of " Thermite," and is largely used for repairing defective castings, broken main shafts, stern-posts of steamers, broken cog-wheels, and for welding tram-lines together, the joints of which, when properly carried out, are equal in strength to the rest of the rail.

Powdered aluminium is extensively used in the preparation of aluminium paint. Its manufacture is a trade secret,

although many suggestions as to methods adopted have been published.

Quite recently a patent has been taken out for an explosive consisting of powdered aluminium and ammonium nitrate, the products of which are alumina, nitrogen, and water.

This explosive will most probably be found of great value for use in coal-mines, as it is quite harmless under ordinary conditions, and the patentee claims that, by varying the proportions of aluminium and ammonium nitrate, any explosive force from that of gunpowder to that of nitro-glycerine can be obtained.

A new application of aluminium which has already become of some importance is as a substitute for stone in lithographic work.

Pure aluminium is a comparatively weak metal, its breaking strain in the form of wire being about thirteen tons per square inch, as compared to thirty tons for hard-drawn copper, and thirty-five tons for steel wire. Hence, where strength is required, the light metal is alloyed with other metals. In most alloys of aluminium an intra-physical change takes place as time goes on, the alloy becoming weaker in tensile strength, the aluminium zinc alloys showing a noticeable change within a year or two.

The lightness of aluminium, its silvery appearance, superiority to silver as regards tarnishing, are all points in its favour of being used for miscellaneous ornamental articles, photographic frames, matchboxes, cooking utensils, and stair rods. A fine frosted surface, suitable for photo frames, can be obtained by dipping the metal into a solution of caustic soda, washing thoroughly, and then dipping in dilute sulphuric acid, and again thoroughly washing.

Certain French and German regiments have been supplied with helmets and water-bottles made of aluminium ; also the metal is being used a lot in army canteen outfits and

camping equipments; and quite recently aluminium boots
have been placed upon the market for use in wet places,
such as dairies.

It is extensively used in the construction of motor-cars,
for gear cases, mud-guards, and bicycle frames. It is also
rapidly replacing the copper pans used in the jam, soap,
and pickle manufactures, as organic acids scarcely attack
aluminium.

In fact, the above are only a few instances of the uses
the metal is being put to; each day its application is being
extended, where lightness and durability are required.

In the case of cooking utensils, care should be taken not
to scrub the articles with washing soda, otherwise the articles
will soon wear away.

Aluminium would make splendid field-guns, that would
be as strong as those in present use, and not one-third of
their weight.

In sheet it would serve admirably for roofings, being far
lighter and more durable than galvanised iron.

Used in place of copper and silver, for the purpose of
coinage, a piece the size of a penny would weigh about the
same as our present farthing.

The same qualities of lightness and hardness also excellently
fit the light metal for beams of delicate balances for the use
of the small weights used by analysts. Being very sonorous,
it would make capital gongs, bells, etc.

The metal enters largely into the construction of aircraft.

In boat-building the use of aluminium has proved a
failure; even the deck plates do not show any degree of
durability. This corrosion of aluminium by sea water and
sea air is attributed partly to the small amount of impurity
in the metal, such as sodium, and partly to the ease with
which electrolytic action is set up when in contact with
other metals. Aluminium of 99 8 per cent. purity, on being
immersed in sea-water for one month (thirty days) lost 0·008

lb. per square foot of surface, the corrosion being about three and a half times that which would have been experienced by mild steel.

So far, a suitable solder for aluminium has not been found. Tin alone gives a fairly good joint. However, the difficulty has been overcome by electro-coating the metal with copper at the place to be united, and then soldering the copper in the ordinary way.   Messrs Cowper-Coles in London and Schoop of Paris have worked out a process on the above lines for the welding of aluminium without any difficulty.

A new method for obtaining a metallic deposit or veneering is described by the United States Consul at Zurich, Switzerland, as an invention of a chemical engineer of that place. The process consists of ejecting the pulverised or melted metal, such as tin, lead, copper, or aluminium, from a special apparatus with such force that the minute particles of the reduced metal adhere in the form of a solid coating of a remarkable homogeneous appearance.   Not only metals, but also plaster, glass, celluloid, wood, or paper may be coated. The metallic vapours are stated to be produced at a temperature of from 250° to 300° C., and are retained in the apparatus under a pressure of 40 to 60 lbs. to the square inch. The great force with which the vapour is emitted from the apparatus, and the fact that it passes through a tube where it is suddenly reduced to a low temperature, admits of the treatment of substances that are highly inflammable, and on which the coating acts as a preservative.

In conclusion, these applications of the metal are only a few of the many uses it will probably be put to in the future. Hence one feels inclined to believe that, just as we have had the stone and iron ages, so we shall have an aluminium age.

CHAPTER VIII.

THE ANALYSIS AND EXAMINATION OF ALUMINIUM WORKS MATERIALS.

1. Bauxite. 2. Red mud. 3. Alumina. 4. Cryolite. 5 Furnace flux. 6. Oil coke, pitch, and carbon electrodes. 7. Producer gas and coal. 8 Metallic aluminium. 9. Aluminium alloys.

1. Bauxite.

Bauxite contains from 39 to 70 per cent. of alumina, the remainder consisting mostly of ferric oxide, combined water, together with smaller amounts of titanium dioxide, silica, organic matter, lime, magnesia, potash, soda, sulphur trioxide, phosphorus pentoxide, and carbonic oxide. Some, such as " French " bauxites, usually contain only silica, oxides of titanium, aluminium, and iron in the hydrated state, together with less than 0·05 per cent. of chalk.

The following are a couple of typical analyses ·—

(A) Sample from North of Ireland, Not dried.		(B) Sample from France Dried at 100° C	
	Per cent		Per cent.
Alumina (Al_2O_3)	= 45·74	Loss on ignition :—	
Ferric oxide (Fe_2O_3) .	= 15·01	Organic matter and	
Lime (CaO)	= 0·18	combined water .	= 12·70
Magnesia (MgO)	= 0·26	Silica (SiO_2) . .	= 2·70
Potassium oxide (K_2O)	= 0·04	Iron oxide (Fe_2O_3) .	= 23 00
Sodium oxide (Na_2O)	= 0 24	Titanium oxide (TiO_2)	= 3·00
Silicon oxide (SiO_2) .	= 10 31	Alumina (Al_2O_3) .	= 58·55
Titanium oxide (TiO_2)	= 4 16	Other constituents, such	
Sulphur trioxide (SO_3)	= 0 10	as lime, magnesia, and	
Phosphorus pentoxide		alkali . . .	= 0·05
(P_2O_5) . . .	= 0 01		———
Moisture (H_2O) .	= 0 84		100·00
Combined water (H_2O)	= 23·19		
	———	The moisture in the raw material	
	100 08	varies from 9 to 14 per cent	

To prepare the sample for analysis it is broken up on a bucking board, passed through a sieve of a convenient size, mixed, the heap divided into four quarters, *a, b, c, d,* as in fig. 8.

Two opposite quarters, *a, d,* or *b, c,* are taken for passing through a smaller holed sieve, the process of mixing, quartering and taking two opposite quarters being repeated until a convenient bulk is obtained, and finally passing through a 40-mesh sieve.

Ten to twenty grms. are taken for determining the moisture, which is done in the usual way by heating in a steam oven until the weight is constant   Loss equals moisture.   For the loss on ignition 2 gms of the dried bauxite are heated in a platinum crucible until the weight is constant.   Loss equals organic matter, carbon dioxide, and combined water.   The remainder of the 10 to 20 gms. of the dried bauxite is further ground on the bucking board, finally grinding sufficient for analysis in an agate mortar until no grittiness can be felt with the fingers, and the finely ground portion is again dried before weighing out for the analysis.   The remainder of the analysis may be done by either of the following methods A or B, method A being for rather an exhaustive examination, whereas method B is more suitable for the usual ordinary works examination
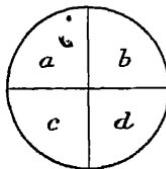
FIG. 8.—Sampling.

METHOD A.—*Modus operandi.*—The bauxite is fused with potassium hydrogen sulphate, the melt extracted with water. Silica determined by volatilising with hydrofluoric acid. Titanium in the filtrate precipitated with sulphur dioxide by boiling, or colorimetrically by means of hydrogen peroxide. Iron and aluminium are then precipitated with ammonia and each determined by any of the usual well-known methods,

The lime and magnesia are separated as oxalate and pho
phate respectively.   Sulphur and phosphorus are determine
in a fresh portion of the ground sample, dissolved in aci
sulphur being precipitated as barium sulphate and tl
phosphorus as phospho-molybdate.

Analysis

Separations of:—Silica (SiO_2).—One gm. of the finel
ground bauxite is mixed with 8 gms of anhydrous potassiu
sulphate in a platinum basin, 4 c.cms. of concentrate
sulphuric acid are added.   The basin is nearly covered wit
a watch-glass and heated gently over a small flame unt
all the water is driven off.   The cover is then remove
and the temperature increased and maintained at a re
heat until everything is quite fluid and clear.   When quit
cold, dissolve the melt out with cold or lukewarm water
The insoluble is filtered off, ignited in a platinum capsule
and weighed.   The insoluble is then moistened with a fev
drops of water and a few drops of sulphuric acid, and ther
evaporated to dryness twice with hydrofluoric acid, ignited
and weighed ; the loss with hydrofluoric acid being silic
(SiO_2).

Titanium Dioxide (TiO_2) —Any residue is fused witl
potassium hydrogen sulphate, and the melt dissolved in cold
or lukewarm water and added to the main solution, which
is then diluted to about 30 fluid ounces and acidified slightly
with sulphuric acid.   Add half a fluid ounce of a saturated
solution of sulphur dioxide, and boil with a cover on for one
hour to precipitate the titanium oxide   The precipitated
titanium oxide is filtered off, washed with hot water, strongly
ignited, cooled, and weighed.   Calculate percentage of TiO_2
on sample dried at 100° C.

Ferric Oxide (Fe_2O_3) *and Alumina* (Al_2O_3).—The filtrate
from the above is concentrated to about 30 fluid ounces
and the iron oxidised with a few drops of nitric acid.   Some

filter-paper pulp can now be added if preferred.   This is prepared by steeping filter paper in concentrated hydrochloric acid until of a pulpy nature, squeezed, and washed well with distilled water   The use of the paper pulp is to facilitate the subsequent filtering of the aluminium and iron precipitate.

The iron and aluminium are now precipitated as hydrates by adding a slight excess of ammonia and boiling for one minute ; filter through a " Buckner " funnel for preference. The precipitate is dissolved in hydrochloric acid and re-precipitated by ammonia as before.   After washing the precipitate with water until the washings are free from sulphates, as tested by acidifying the washings with hydrochloric acid, adding barium chloride and warming, a white precipitate indicates presence of sulphates.

The precipitated hydrates of iron and aluminium are carefully dried and ignited in a muffle furnace, after which it is heated at as high a temperature as possible over a blow-pipe flame,[1] and the mixed oxides weighed as soon as cold, the cooling having taken place in a desiccator.   Weight of mixed oxides of aluminium and iron call weight "M."

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[1] The Teclu burner furnishes a flame of much higher temperature than that produced by the ordinary Bunsen burner.   The air-supply
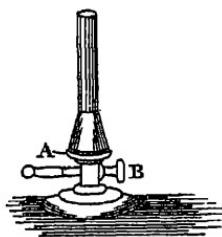
Fig. 9.—Teclu Burner.

enters the conical portion of the burner, and is regulated by rotating the disc (A).   The screw (B) regulates the supply of gas   This burner may be used as a substitute for the foot blowpipe when igniting alumina

The precipitated oxides are next digested in warm hydrochloric acid until all the iron goes into solution. If difficulty is experienced in effecting this, then first fuse the mixed oxides with fusion mixture (sodium and potassium carbonates) and then dissolve the melt in hydrochloric acid. Then the iron in solution is reduced by adding stannous chloride solution drop by drop until all colour due to iron in the ferric state is discharged and the whole cooled. Just before titrating, dilute somewhat with recently boiled distilled water which has been cooled.

The excess of stannous chloride is oxidised by the addition of a slight excess of mercuric chloride, and the iron then titrated with a standard solution of potassium bichromate (1 c.cm. = about $0·01 Fe_2O_3$). The weight of ferric oxide is deducted from the weight of mixed aluminium and iron oxides (M) to obtain the weight of alumina. These are then converted into percentages on the sample dried at 100° C. Or, if desired, the aluminium and iron may be separated and both determined gravimetrically, thus : add the solution of mixed oxides in the hydrochloric acid to an excess of warm sodium hydrate solution, digest some time on a warm plate, and filter off the hydrated ferric oxide, washing the precipitate thoroughly.

The precipitate of ferric hydrate should be dissolved in hydrochloric acid and reprecipitated by means of an excess of ammonia, filtered, and washed with water until free from chlorides. This reprecipitation is necessary to free the precipitate from the caustic alkali which is retained in the first precipitation. The ferric hydrate is then ignited and weighed as ferric oxide (Fe_2O_3).

The alkaline filtrate from the first precipitation of the iron is acidified with hydrochloric acid, warmed up to about 70° C., a slight excess of ammonia (say half a c.cm. of 1 . 1 ammonia in excess) added, and the whole boiled for one minute. The aluminium hydrate is filtered, washed, ignited,

and weighed in the same manner as the mixed oxides of iron and aluminium (M), pulp paper being used if desired. Alumina = Al_2O_3.

Lime (CaO).—The filtrate from the mixed iron and aluminium hydrates is brought to the boil, made strongly ammoniacal, and ammonium oxalate added in excess with constant stirring, and allowed to stand for three or four hours to cool and allow the precipitate of calcium oxalate to settle out.

The precipitate of calcium oxalate is then filtered off and washed with cold water containing about 2 per cent. of ammonia. The precipitate of calcium oxalate is dried and ignited, gently at first, finally heating strongly at a bright red heat for twenty to thirty minutes. Cool in a desiccator and weigh as lime (CaO).

Magnesia (MgO).—The filtrate from the calcium oxalate is evaporated to dryness, with the addition of nitric acid at intervals to destroy the bulk of ammonium salts. When cold, dissolve in water, using a little hydrochloric acid if necessary, and make strongly ammoniacal. Then add an excess of ammonium phosphate solution, drop by drop, with constant stirring, and allow to settle, say, for about six hours, after which filter, and wash free from excess of phosphate with 8 per cent. ammonia water. The precipitate, dry, ignite at a moderate red heat, and weigh as $Mg_2P_2O_7$. Calculate to per cent. of MgO.

Alkalies (K_2O,Na_2O).—I have found the "Lawrence-Smith" method for the determination of the alkalies in bauxite to give satisfactory results, provided sufficient excess of hydrate or carbonate of lime be used to prevent the mass from fusing, the procedure being as follows :—

Weigh accurately about 5 gms. of the finely powdered bauxite into a platinum crucible. Mix this with 5 gms. of pure recrystallised ammonium chloride and 20 gms., or sufficient to prevent fusion, of pure calcium carbonate.

Heat the crucible just to bright redness for an hour. This may be effected by a good Bunsen flame or blowpipe, or the platinum crucible may be placed in a clay crucible containing a little calcined magnesia or lime at the bottom and round the sides, and then heated in a gas furnace. Place the cold platinum crucible and its contents in hot water in a covered platinum or porcelain crucible and boil for a time. This procedure will dissolve out the alkaline chlorides together with some calcium hydrate Filter, and mix the filtrate with ammonium hydrate and ammonium carbonate in excess, and then add a few drops of ammonium oxalate. Stir well and allow to stand. Filter into a platinum or porcelain dish, evaporate the filtrate to dryness, and heat the residue *short* of redness, but sufficiently strongly to drive off the ammoniacal compounds. Dissolve the residue in water, and add a few drops of ammonium hydrate and ammonium oxalate solutions in order to precipitate any traces of calcium which may still remain in the solution Filter, add a few drops of hydrochloric acid to the filtrate, and evaporate it to dryness in a weighed dish. Ignite the residue gently and weigh it, repeating the ignition until the weight is constant.

The weight of the residue gives the weight of potassium and sodium chlorides. If this be small, it may be presumed to be all sodium chloride for ordinary purposes.

$$2NaCl = Na_2O$$
$$2(23 \cdot 05 + 35 \cdot 45) = (46 \cdot 1 + 16)$$
$$\therefore \qquad Factor = 1 = 0 \cdot 530\ 85.$$

Calculate percentage of sodium oxide, Na_2O.

The respective amounts of sodium and potassium oxides may be determined by any of the following methods :—

(a) By determining the potassium chloride and taking the sodium chloride by difference, and calculating the potassium chloride and sodium chlorides to oxides. (b) Or by

determining the chlorine and calculating the respecti
quantities of potassium and sodium that will equal t
chlorine, the latter being determined either gravimetrical
or volumetrically. (c) The mixed chlorides after weighin
are converted into sulphates and weighed, and the pota
sium and sodium chlorides calculated from the increa
in weight.

(a) The weighed residue is dissolved in water and a fe
drops of hydrochloric acid added, then an excess of platinu.
chloride solution. The liquid is then evaporated on a wate
bath, and the residue is treated with alcohol, in which th
potassium salt K_2PtCl_6 is insoluble. Allow the precipitat
to settle completely, and filter through a tared filter. Was
the precipitate upon the filter with alcohol until the washing
are no longer coloured, then dry the filter and its content
at 100° C. When dry, weigh
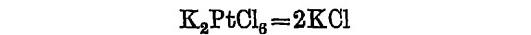
$$K_2PtCl_6 = 2KCl$$
$$39.15 + 39.15 + 194.8 + 212.7 = 78.3 + 70.9$$
$$\therefore \quad 1 = 0.307\ 12.$$
$$2KCl = K_2O$$
$$1 = 0.632\ 04.$$
$$K_2PtCl_6 = K_2O$$
$$\therefore \quad 1 = 0.1941.$$
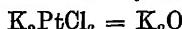
(b) The determination of the chlorine may be done eithe
(1) gravimetrically or (2) volumetrically.

(1) The weighed chlorides are dissolved in dilute nitri
acid, and then excess of silver nitrate added. Warm som
time, taking care not to boil. Wash the precipitate in the
beaker by decantation three times with hot water containing
a little nitric acid, then transfer it to a filter and continu
the washing with water acidified with nitric acid, and finally
with hot water only, until a drop of hydrochloric acid added
to the filtrate produces no turbidity. Dry the precipitate
in the steam oven. The dry precipitate is turned out upor

A

a piece of glazed paper and is covered with a funnel. The filter is then folded, and its upper edges, which are free from silver chloride, are held in the flame by means of the crucible tongs. The ash thus produced is allowed to drop into the crucible. The ash is then treated with nitric acid and with hydrochloric acid, and is dried by evaporation. The precipitate is finally transferred to the crucible, and is ignited with the ash; cool and weigh

$$AgCl = Cl$$
$$1 \; : \; 0.247\ 24.$$
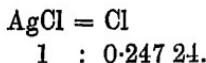
(2) Volumetrically the chlorine may be determined by titration with a standard solution of silver nitrate. $\dfrac{1}{100}$ normal silver nitrate solution is a convenient strength to use, which is made by dissolving $1.699\ 8$ gms. $AgNO_3$ in a litre of water. Each c.c. of this solution corresponds to $0.000\ 354\ 5$ of Cl.

The weighed potassium and sodium chlorides are dissolved in water, a few drops of potassium chromate added to serve as indicator, which gives a permanent red colour due to silver chromate as soon as all the chloride is precipitated by the silver nitrate. The neutral solution of the chlorides is then titrated with the standard silver nitrate solution until the red colour is just permanent on stirring.

The weights of sodium and of potassium present in the residue may then be calculated from the following formulæ :—

$$\text{Weight of K} = \frac{[(A - B) \times 1.54] - B}{0.63}$$

$$\text{Weight of Na} = \frac{B - (A - B) \times 0.91)}{0.63}$$

where   A = the weight of the mixed chlorides, and
         B = the total weight chlorine in the chlorides.

The potassium and the sodium are then calculated to oxide.

$$2K = K_2O$$
$$\therefore \quad 1 = 1\cdot204.$$
$$2Na = Na_2O$$
$$\therefore \quad 1 = 1\cdot347.$$

(c) The weighed mixture of potassium and sodium chlorides is moistened with a slight excess of sulphuric acid. Take to dryness, ignite, and weigh.

Then, as the ratio of the weights

$$2NaCl : Na_2SO_4$$
$$117\cdot02 : 142\cdot18 = 1 : 1\cdot215$$

and

$$2KCl : K_2SO_4$$
$$149\cdot18 : 174\cdot34 = 1 : 1\cdot169$$

from 1 gm. of an unknown mixture of the two chlorides the weight S of the mixed sulphates is obtained, there holds the equation :—

$$1\cdot215\,x + 1\cdot169\,(1 - x) = S$$

and

$$x = \frac{(S - 1\cdot169)}{0\cdot046}.$$

Where $x =$ weight of NaCl.

For the estimation of the phosphorus and sulphur, weigh accurately 2 gms. of the sample, dissolve in aqua regia, take to dryness with hydrochloric acid to drive off the nitric acid. Take up with hydrochloric acid and water, add a small excess of ammonium hydrate, filter, and wash. To the acidified filtrate add barium chloride, and eventually collect the barium sulphate and weigh.

$$BaSO_4 = S$$
$$1 \quad : 0\cdot137\ 32.$$

The ammonia precipitate contains the iron, titanium, silica, and aluminium with the phosphorus. It is dissolved in

hydrochloric acid, taken to dryness, taken up with hydrochloric acid and water, and filtered.

The iron is then reduced by passing sulphur dioxide through the solution, and the basic phosphate of aluminium is now precipitated either with a slight excess of ammonia or with calcium carbonate The resulting precipitate is fused with sodium carbonate, the mass digested with water, and any oxide of iron or sodium titanate filtered off. The phosphorus in the filtrate may be collected by adding a little ferric oxide, precipitating as ferric phosphate by adding a slight excess of ammonia, dissolving the precipitate in nitric acid. Add 2 to 3 gms. of $AmNO_3$, make just ammoniacal, then just acid with nitric acid, adding 2 c cs. in excess, then 50 c.cs. of the following ammonium molybdate solution, taking care to keep the portion containing the phosphorus below 100 c.cs.

Preparation of the Ammonium Molybdate Solution.—Pour 100 c.cs. of water into a large flask, add 50 gms. of molybdic acid, and then 100 c.cs. of the strongest ammonia solution Stir the liquid until all the solid is dissolved, then pour the solution quickly into 720 c.cs. of cold strong nitric acid, stirring during the addition. Keep the liquid in a warm place for some hours, and decant the clear solution for use.

The solution containing the precipitated phosphorus is warmed at about 30 to 35° C. for about half an hour. Filter, washing with cold water containing 2 per cent. nitric acid, and finally with one wash of plain cold water. It is then dried at 120° C. on a tared filter and weighed as $(NH_4)_3 11MoO_3 PO_4$, containing 1·63 per cent. of phosphorus.

METHOD B.

The second procedure is quicker and more suitable for routine analyses required in a works.

Modus operandi.—The constituents of the bauxite are converted into sulphates, diluted to a known volume, and

an aliquot portion taken, from which the iron, aluminium and titanium are separated by means of ammonia. The lime and magnesia in the filtrate are separated with ammonium oxalate and ammonium phosphate respectively The final filtrate is taken to dryness with nitric acid to destroy ammonia salts, and the residue converted into sulphate and weighed as Na_2SO_4.

Sulphur and phosphorus seldom occur in more than mere traces, so that these are usually not determined in every sample.

The titanium is determined colorimetrically in a portion of the original solution by the yellow colour produced on adding an excess of hydrogen peroxide. Another portion of the original solution is reduced by hydrogen sulphide or sulphur dioxide, and the reduced iron titrated with standard potassium permanganate.

Instead of determining the titanium by colour, it may be done volumetrically together with iron by reducing both with zinc in acid solution and then titrating. The difference between the titrations of solutions reduced by zinc and sulphuretted hydrogen respectively will be due to the titanium.

Method —Digest 2 gms. of the finely powdered dried bauxite with 30 c.cs. of water and 30 c cs. of concentrated sulphuric acid in a covered beaker on a warm plate until the ore is all attacked, gradually increasing the temperature for two to three hours Remove the cover and evaporate until dense white fumes are given off, cool, and dilute to about 250 c.cs. with water, bring to the boil, and continue boiling until all the soluble salts have gone into solution Solution is complete when all the silky appearance due to the aluminium sulphate has disappeared and only silica appears to remain. The solution is filtered, preferably through a double Schleicher and Schull, No. 589, 11-cm. black-band filter paper.

The insoluble matter is washed with hot water until free from sulphates, ignited, and weighed in a platinum capsule or crucible.

Silica (SiO_2).—A few drops of water and sulphuric acid are added, and the silica volatilised by means of hydrofluoric acid, again ignited, cooled, and weighed   The loss is equivalent to silica.

If there is any appreciable amount of residue left after treating with hydrofluoric acid, fuse with potassium hydrogen sulphate, cool, and dissolve in lukewarm water, the alumina and titanium oxide being determined in the same manner as in the filtrate from the silica.

If the alkalies are to be determined, then the above solution must not be added to the main solution, but the alumina and titanium determined separately.   But if the alkalies are not being determined in the main solution, then add the solution from the potassium hydrogen sulphate fusion to the main solution, and make the whole bulk up to exactly 500 c.cs

As a rule, the insoluble from the silica consists of about two-thirds titanium oxide and one-third alumina, but generally, if the conversion into sulphates is carried out properly, there is seldom more than a trace of residue left after treating with hydrofluoric acid.

After making up the main solution from the silica to 500 c.cs. (exactly) with water, aliquot portions are taken for the following determinations ·—

Measure off exactly 100 c cs. (equal to 0·4 gm. of the original dried sample) of this solution, bring to the boil, add a few drops of nitric acid, cool to about 80 ° C., add a slight excess of ammonia (1 : 1), with constant stirring, then boil for one to two minutes, and immediately filter.

The precipitated hydrates of aluminium, iron, and titanium filter best before they have time to clot, hence immediate filtration is recommended.   The precipitate is washed with

hot water until the washings are free from sulphates. Tl precipitate is ignited at a red heat, and finally at a whi heat over the blowpipe flame, cooled in a desiccator, ar the mixed Al_2O_3, Fe_2O_3, and TiO_2 weighed as soon as col Repeat the heating until the weight is constant.

To determine the iron, measure another 100 c.cs. of tl main solution (that was made up to 500 c.cs.) into a 400-c. conical flask, and reduce the iron by passing a rapid stream sulphuretted hydrogen through the solution until saturate A small funnel is placed in the neck of the conical flask, ar the excess of sulphuretted hydrogen boiled off. When all tl excess of sulphuretted hydrogen gas is driven off, the stea will not blacken a piece of paper moistened with lead acetat The solution is cooled rapidly and titrated with potassiu permanganate solution (1 c c. $= 0.005Fe_2O_3$).

Preparation of Standard Potassium Permanganate Soli tion.—The following reaction takes place when a *cold* acid fied solution of ferrous salt is used in the titration :—

$$K_2Mn_2O_8 + 10FeSO_4 + 9H_2SO_4 = 5Fe_2(SO_4)_3$$
$$+ 2MnSO_4 + 2KHSO_4 + 8H_2O.$$
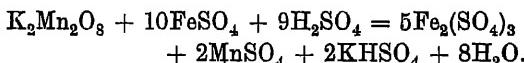
$$\therefore \quad K_2Mn_2O_8 = 5Fe_2O_3$$
$$316.3 = 799.$$

As the permanganate solution is required to be abou equal to 0.005 gm. Fe_2O_3 per c c, 1 000 c.cs. will equ about 5 gms. Hence if 2 gms. of $K_2Mn_2O_8$ be dissolve in a litre of water, 1 c.c. will approximately be equivaler to 0.005 gm. Fe_2O_3.

The exact strength of the solution is ascertained by di solving 0.980 gm. of pure ferrous ammonium sulphate i water with a few drops of sulphuric acid and titrated wit the potassium permanganate solution until a slight pin permanent colour is produced.

$Fe(NH_4)_2(SO_4)_2,6H_2O$, contains $\dfrac{1}{7}$ its weight of iron,

hence 0·98 gm. $Fe(NH_4)_2(SO_4)_2,6H_2O - 7 = 0·14$ gm. Fe,

and $\qquad$ 0·14 Fe $\times \dfrac{10}{7} = 0·2$ gm. of Fe_2O_3.

$\therefore \quad \dfrac{0·2 \text{ gm.}}{\text{c c. } KMnO_4} =$ weight of Fe_2O_3 each c.c. $KMnO_4$ will

equal.

Determination of the Titanium Oxide —Ten to twenty c.cs. of the main solution are transferred to a Nessler tube, hydrogen peroxide is added until the yellow colour produced does not become any deeper in intensity. The same quantity of hydrogen peroxide is put into another Nessler tube, some water added, and standard solution of titanium solution run in until the colour in both tubes is identical, the bulk of each tube being the same   Calculate to TiO_2.

Preparation of Standard Titanium Solution.—Weigh accurately 0·8 gm. of pure titanium dioxide into a platinum crucible, add 10 gms. of pure potassium hydrogen sulphate, and heat over a small flame until the bisulphate is melted, taking great care to prevent any frothing over the side of the crucible. Fumes of sulphur dioxide should be evolved, and the mass kept liquid, the crucible bottom never being allowed to get above a dull red heat. When solution is complete, tilt the crucible on to one side at an angle of about 45°, and cool. When quite. cold, dissolve out with about 100 c.cs. of one to three ($1H_2SO_4$. 3 water) sulphuric acid, and finally make up the whole bulk to 2 litres.

One litre may be taken, and the titanium contents determined [by precipitation with sulphur dioxide, as described on page 44.

Each c.c. ought to equal 0·000 4 gm. TiO_2, and if 2 gms. of the original sample be taken and made up to 500 c.cs , of which 10 c.cs. be taken for the determina-

tion, then each c.c of titanium solution will equal per cent. TiO_2.

The TiO_2 and Fe_2O_3 are deducted from the combined weight of Al_2O_3, Fe_2O_3, TiO_2, to obtain the Al_2O_3 by difference.

The filtrate from the ammonia precipitate (the precipitate containing the $Al_2O_3,3H_2O$, $Fe_2O_3,3H_2O$, and hydrated titanium oxide) is brought to the boil, ammonium carbonate and a little ammonium oxalate added, and the whole allowed to cool. The calcium oxalate is filtered off, washed with 2 per cent. ammonia water, ignited strongly, and weighed as calcium oxide, CaO.

The filtrate from the precipitate of calcium oxalate is taken to dryness with nitric acid, so as to get rid of the ammonium salts, finally heating to a dull redness Moisten with a slight excess of sulphuric acid, heat to drive off the excess of acid, and weigh as sodium sulphate, Na_2SO_4. Calculate to Na_2O.

$$Na_2SO_4 \cdot Na_2O$$
$$1 \quad : 0.4368.$$
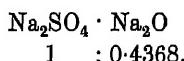
When a rapid approximate determination of the alumina contents is required, that of Gatenby's volumetric method is useful.   The method is based upon the fact that alumina is indifferent to methyl-orange, but acid to litmus solution.

The alumina is digested out by means of caustic soda solution, filtered, and the free soda in the filtrate titrated in the cold with normal hydrochloric acid (number of c cs. required = " A "), using phenolphthalein as indicator.   Then add a few drops of methyl-orange, and again titrate with $\frac{N}{1}$HCl, with constant stirring, until the pink colour is permanent, for a few seconds. (Total number of c.cs. taken = " B.")

Then, reading of burette " B " minus reading of burette

" A " equals " C," number of c.cs. $\dfrac{N}{1}$ acid by the sodiun aluminate, and alkaline salts. Litmus is then added a: indicator, and the solution titrated back with $\dfrac{N}{1}$ causti< soda solution until there is a decided blue colour. Numbe: of c.cs. $\dfrac{N}{1}$ NaOH required call " D." Then, number o c.cs. " C " minus number of c.cs. " D " gives the c.cs $\dfrac{N}{1}$ acid required by the alumina.

$$1 \text{ c.c. } \dfrac{N}{1} \ldots \text{ solution} = 0 \cdot 020\ 57 \text{ Al}_2\text{O}_3.$$

A factor found by experiment and pointing to the sal as $Al_2O_3 : 5$ HCl.

2. Red Mud.

The analysis of red mud may be done in the same wa} as bauxite method A (p. 43), except that it is advisable t< check the alumina contents by redissolving the aluminium and iron hydrates which are precipitated by ammonia, ir acetic acid, reducing the iron by boiling with an excess o " hypo " ($Na_2S_2O_3,5H_2O$, dissolved in water), and add 5 c.cs of a saturated solution of sodium phosphate, and then 5 gms of sodium acetate dissolved in a little water. Boil until th< solution smells no longer of sulphurous acid. Filter, wash dry, and ignite, and weigh as aluminium phosphate, $AlPO_4$.

$$2AlPO_4 = Al_2O_3$$
$$244 \cdot 2 = 102 \cdot 2$$
$$\therefore \qquad\qquad 1 = 0 \cdot 418\ 4.$$
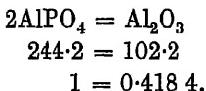
The following is a typical analysis of a sample of " Rec Mud " —

Moisture	.		.	.	.	39·42	per cent
Combined water		.	.	.		4·24	,,
Silica	.	.	.	.	.	3·52	,,
Ferric oxide		.	.	.	.	37·57	,,
Titanium oxide	.		.	.		4·55	,,
Alumina	.	.	.	.	.	7·00	,,
Sodium oxide		.	.	.	.	3·67	,,

99·97 per cent.

3. The Analysis of Purified Alumina.

The alumina obtained from bauxite by the Baeyer's process is usually exceptionally pure. The impurities alone are determined, and the alumina taken by difference

For the moisture 10 gms. are heated at 100° C. until the weight is constant.

To determine the combined water, 2 gms. of the dried material are heated over an Argand burner, and the temperature very gradually raised; otherwise, if the temperature be raised too rapidly, spitting occurs. The temperature is finally raised to almost a white heat for twenty minutes, using a blowpipe flame if necessary. Weigh as soon as cold.

Estimation of Silica.—Two gms. are fused with fusion mixture, or potassium bisulphate, the melt dissolved in water, 10 c cs. of sulphuric acid added, and the solution evaporated until dense white fumes are evolved. Dilute with water, and boil until all the sulphates are dissolved. Filter and wash with water till free from sulphates. The insoluble residue ignite and weigh. Volatilise the silica by adding hydrofluoric acid and one or two drops (1 . 3) sulphuric acid, and evaporating to dryness, ignite, and weigh. The loss will be silica, SiO_2.

Estimation of the Iron.—To the main solution (the filtrate from the insoluble in sulphuric acid) add 10 to 12 gms. of tartaric acid, and when dissolved make the solution ammonia-

cal   A rapid stream of sulphuretted hydrogen is then passed
through the solution, and the precipitated ferrous sulphide
rapidly filtered off.   Dissolve the precipitate in a few drops
of hydrochloric acid, and dilute to a convenient bulk in a
Nessler tube, then add an excess of potassium thio-cyanate.

The same amount of potassium thio-cyanate solution is
added to a similar Nessler tube, one or two drops of hydro-
chloric acid added, and standard iron solution added from a
burette (1 c.c. $= 0.000 \cdot 1$ gm Fe_2O_3) until the depth of red
colour in both solutions is the same, and the bulk of each
equal

Estimation of the Lime (CaO) *and Soda* (Na_2O).—For the
lime and soda determination boil 2 gms of the alumina with
about 100 c.cs. water containing a few drops of hydrochloric
acid, and filter through a double black-band Schleicher
and Schull, No. 589, filter paper.   Repeat with successive
amounts of acidified water two or three times.   The com-
bined filtrates evaporated to a low bulk, and made just
ammoniacal, boil and filter off any hydrate of alumina , more
ammonia is added to the filtrate, ammonium carbonate added,
the solution brought to the boil, then take off the boil, add a
few drops of ammonium oxalate, stir well, and allow to stand
to cool and the precipitate has settled out—usually a couple
of hours.   Filter, washing the precipitate with ammoniacal
water, ignite, and weigh as lime, CaO.

The filtrate is evaporated to dryness, very gently heated
to a very dull red heat to drive off all the ammonium salts ;
add one or two drops of sulphuric acid, dry, and ignite at
a red heat to drive off the excess of acid ; cool, weigh as
Na_2SO_4.

$$Na_2SO_4 = Na_2O$$
$$1 \quad : \ 0.436\ 83$$
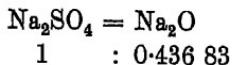
The hydrate of alumina is done in the same way as alumina,
except for the silica and iron portion.   Solution is effected by

dissolving in hydrochloric acid, and then taking to fuming with sulphuric acid, and proceeding as with alumina

It is advisable to do a " blank " portion alongside so as to determine the silica, iron, lime, and soda in the reagents used, which ought to be deducted from that found in the sample portion.

Density.—This is a most important determination, as the ordinary amorphous alumina, the α, has a density of from 3·38 to 3·52, and takes up mois-ture readily. This, on being heated to over 1 000° C., gradually changes into a crystalline form, denoted by β, having a density of about 3·8, which is non-hygroscopic, hence it can be transported by sea without any appreciable amount of mois-ture being taken up.

Method of determining the density :—

Blount's method as applicable to cements is very suitable for this purpose.

A " Blount's " flask " A " (fig. 10) (which is of about 70 to

Fig 10.—Apparatus for Determining Density.

75 c.cs. capacity ; the c.cs from 64-c.c. mark to the 67-c.c. mark are graduated on the neck) is attached to a 60-c c. burette "B," which is inserted within the outer jacket of a Liebig's condenser "C." Cold water enters at "D," circulates around the burette, and then down the tube " E " and out of the cooling tank " F " by the outlet " G," as shown in the accompanying diagram.

To proceed with the determination . the burette is filled up to the 60-c c. mark with petroleum ether, or ligroin, with a boiling-point of from 80° to 100° C. About 40 c.cs. of this is run into the clean dry flask. The flask and liquid

are carefully and quickly weighed, and then about 22 gms. of the alumina whose density is to be determined are shaken in the flask to remove all the air bubbles, and weigh again. The flask is connected to the burette and the remainder of the 60 c.cs. petroleum added, and the volume read off on the neck of the flask.

The total volume, minus 60 c.cs., will equal the volume occupied by the number of grammes of material weighed off.

$$\therefore \quad \frac{\text{Weight of alumina taken}}{\text{volume occupied by the alumina}} = \text{density as compared with water.}$$

As precipitated under the usual conditions in the Baeyer process, the hydrate contains about 49 per cent. of alumina, a typical analysis of the calcined alumina being—

Moisture	0·330	per cent.
Combined water	0·500	,,
Silica	0·150	,,
Ferric oxide	0·007	,,
Sodium oxide	0·300	,,
Lime	0·013	,,
Alumina (by difference)	98·700	,,

4. Cryolite.

The following method has been found to work satisfactorily, and perhaps the procedure may best be shown by an actual example.

Moisture.—0·844 8 gm. of finely powdered cryolite was thoroughly mixed with about 5 gms. of recently ignited lead oxide (litharge, PbO) powdered, the crucible and contents heated in a water oven until the weight was constant.

Weight of crucible, cryolite, and lead oxide = 17·850 7 gms.

,,   ,,   ,, after heating = 17·825 5 ,,

Moisture   .   .   .   .   .   .   0·025 2 gms.

Sodium.—0·3 gms of sample and 0·7 gm. of calcium carbonate were ground together in an agate mortar, and the mixture then transferred to a platinum crucible and ignited over a Bunsen flame for forty-five minutes and then over a blast blowpipe flame for fifteen minutes.   The sintered mass was placed in a porcelain dish, hot water added, the solution acidulated with acetic acid and evaporated to dryness over an Argand burner.   The evaporation with acetic acid was repeated and the residue heated till all free acid had been driven off, when hot water was added and the solution boiled for a few minutes, and filtered.   (Residue was reserved for the fluorine determination.)

To the filtrate, ammonium carbonate was added and the precipitated calcium carbonate filtered off.   Nitric acid was added to the filtrate, the solution taken to dryness, and the residue heated till ammonia compounds ceased to be given off.   The residue was extracted with boiling water, and the solution taken to dryness with slight excess of sulphuric acid.   The residue of Na_2SO_4 was taken up with hot water made alkaline with ammonium carbonate, the solution filtered into a weighed platinum dish, the filtrate taken to dryness, and strongly ignited over a blast blowpipe   Two checks were made by the method, 0·5 gm. of cryolite and 1·0 gm. of calcium carbonate being employed

1. Sodium   .   .   .   .   .   32·73 per cent.
2.   ,, ...   32·61   ,,

Fluorine.—The residue left after acetic acid treatment contained the whole of the fluorine, which was estimated as follows :—

The residue was fused with bisulphate of soda (about ten times the weight of CaF_2), the fused mass taken up with dilute hydrochloric acid and diluted to 500 c.cs   250 c.cs. were taken for the estimation of the contained lime.   The solution was made alkaline with ammonia and the precipi-

tated aluminium, hydrate filtered off, redissolved and repre-cipitated with ammonia, and filtered. The two filtrates were mixed and the lime precipitated as oxalate, dried, ignited finally over the blowpipe flame for fifteen minutes at a bright red heat, cooled, and weighed as CaO.

$$CaO = CaF_2$$
$$1 \quad : \quad 1.392.$$
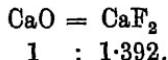
Two check results gave :—

1. Fluorine .   .   .   .   50·30 per cent.
2.   ,, ... 50·30   ,,

In all three estimations 0·5 gm. of cryolite was taken for analysis.

Aluminium —2 gms. of cryolite were fused with about 14 gms. of bisulphate of soda, the fused mass taken up with dilute hydrochloric acid, and the solution diluted to 500 c.cs. 100 c.cms. were taken for the estimation.

The alumina was precipitated with ammonia, the precipi-tate redissolved in hydrochloric acid, and the alumina repre-cipitate ignited and weighed

No 1. Aluminium   .   .   . 12·69 per cent.
No. 2.   ,,   . ·   .   . 12·45   ,,

As a further check the alumina obtained during the estima-tion of the fluorine was ignited and weighed.

12·51 per cent. aluminium.

Silica.—2 gms. of the sample together with 20 to 30 c cs. of strong sulphuric acid were transferred to a small platinum still connected with a " U " tube (also of platinum) containing potassium acetate. The contents of the still were heated to 150°–160° C. for four hours, a current of dry air being drawn through the still during the whole of the operation. The contents of the " U " tube were then

dissolved in 50 per cent. alcohol and the precipitated potassium silico-fluoride allowed to stand several hours, filtered off, washed with 50 per cent. alcohol, then dissolved in hot water and titrated with N/10 alkali, using phenolphthalein or litmus.

$$3SiF_4 + 3H_2O = 2H_2SiF + H_2SiO_3.$$

$$K_2SiF_6 + 4KOH = 6KF + SiO_2 + 2H_2O.$$
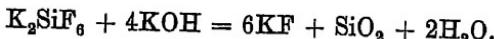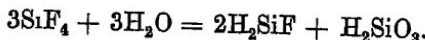
Hence $1 \text{ c.c. } \dfrac{N}{10}KOH = 0\cdot113\% \ SiO_2.$

Since 2 gms. were taken and only two-thirds of the original SiO_2 are filtrated.

Fig. 11 is a sketch of the apparatus for the silica determination :—
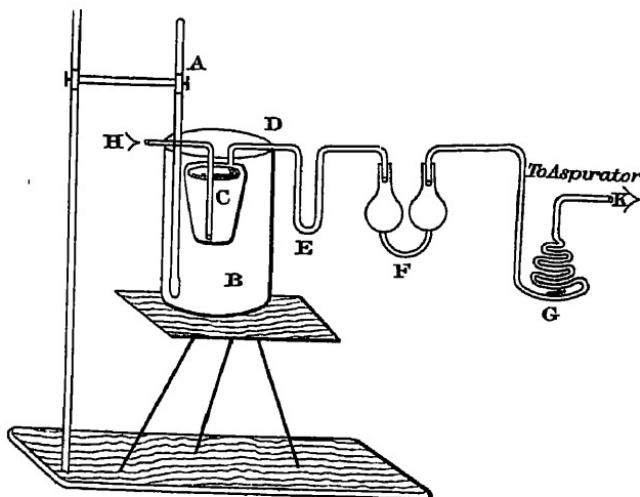
Fig. 11.—Apparatus for Silica Determination.

A is the thermometer, B a tin supported on a tripod over a Bunsen burner, C is the platinum still containing the cryolite and sulphuric acid. The lid with tube D is

κ

securely fastened to the still C and the platinum " U " tube E with rubber solution.

E contains the potassium acetate, F is a glass " U " tube containing lumps of calcium chloride, and G is a worm containing concentrated sulphuric acid ; " U " tubes containing drying materials are attached to H, and a gentle stream of dry air is drawn through the apparatus from H to K by means of an aspirator.

Ferric Oxide.—One estimation was made upon the material left in the platinum still from the estimation of the silica. The sulphuric acid solution was diluted to about 200 c.cs., the ferric sulphate reduced by sulphuretted hydrogen, and, after boiling off the excess of sulphuretted hydrogen and cooling, the ferrous sulphate was titrated with standard potassium permanganate solution.

Ferric oxide $= 0.22$ per cent.

A second estimation was made with 250 c.cs of the solution used for estimation of aluminium (bisulphate fusion)

Ferric oxide $= 0.19$ per cent.

Magnesia.—2 gms. of sample were fused with about 5 gms. of sodium carbonate, the fused mass extracted with water, and the solution diluted to 500 c cs.   100 c.cs. were boiled, acidified with hydrochloric acid, ammonium carbonate added, and the alumina filtered off, dissolved in hydrochloric acid, and reprecipitated.   The two filtrates were mixed, concentrated, ammonium oxalate added, and the solution allowed to stand over night.   No precipitate appearing, ammonium phosphate and a large excess of ammonia were added, and the solution again allowed to stand over night.   Filtered, ignited, and weighed precipitate.
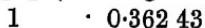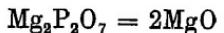
$$Mg_2P_2O_7 = 2MgO$$
$$1 \qquad \cdot \ 0.362\ 43$$
Magnesia $= 0.19$ per cent.

Zinc.—2 gms. of sample were fused with 8 gms. of sodium carbonate, and the fused mass dissolved in water acidulated with hydrochloric acid. The alumina was precipitated as basic acetate, the precipitate dissolved in hydrochloric acid, and the alumina reprecipitated by ammonium hydrate The filtrates were mixed and the solution evaporated down to about 150 c.cs., which were transferred to a flask, ammonium chloride added, and the solution made slightly alkaline with ammonia. About 2 c.cs. of ammonium sulphide solution were added, the flask filled up to the neck with water, corked, and allowed to stand over night in a warm place, filtered, ignited, and weighed as oxide.

Zinc . . . . . . 0·13 per cent.
equal to zinc sulphide . . . 0·19 ,,

The zinc was also determined as follows :—

5 gms. of cryolite were boiled with concentrated hydrochloric acid, diluted, and filtered. Filtrate made alkaline with a good excess of pure caustic soda, boiled, and filtered, a rapid stream of sulphuretted hydrogen passed through the solution, the precipitate filtered, and dissolved in hydrochloric acid and made ammoniacal, boiled, and any alumina filtered off.

The filtrate was again made alkaline and suphuretted hydrogen passed through the solution, the zinc sulphide filtered, burnt to oxide, and weighed.

$$ZnO = Zn$$
$$1 \quad . \quad 0·803\ 44$$
$$Zinc = 0·15 \text{ per cent.}[1]$$

Sulphuric Anhydride.—100 c.cs of the sodium carbonate solution (see estimation of MgO) were boiled, ammonium

[1] Some glass beakers have some zinc in their composition, which are attacked in the above determinations of zinc, probably due to the action of the fluorine. This was found to be the case with some new beakers.

carbonate solution added, the alumina filtered off, and the
filtrate freed from all ammonia by boiling, a few c.cs. of
a solution of sodium carbonate added to the filtrate, the
solution boiled, and boiling calcium chloride solution added.
The precipitate ($CaCO_3, CaF_2$) was filtered off, washed with
hot water, and the filtrate and washings preserved. The
precipitate was ignited in a porcelain crucible and the
residue taken to dryness with (twice) acetic acid. Taken up
with hot water, filtered, and washed insoluble portion with
hot water, till free from sulphates. The two filtrates were
then mixed, acidified with hydrochloric acid, the solution
boiled, and the SO_3 precipitated by barium chloride, filtered,
washed, ignited, and weighed as $BaSO_4$.

$$BaSO_4 = SO_3$$
$$1 \quad : \quad 0.342\ 93$$
Sulphuric anhydride = 1.26 per cent.

A check estimation gave :—

Sulphuric anhydride = 1.19 per cent.
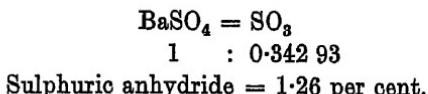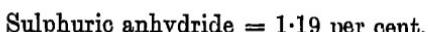
Constituents Soluble in Water.—5 gms. of the cryolite
were boiled with about 250 c.cs. of water, the insoluble
filtered off, and the filtrate diluted to 500 c.cs. A pre-
liminary examination showed sodium oxide to be the only
base present, and sulphuric anhydride the only acid radicle
in solution.

Sodium Oxide.—100 c.cs. were acidulated with sulphuric
acid, the solution taken to dryness in a platinum dish, and
the residue strongly ignited and weighed.

$$Na_2SO_4 = Na_2O$$
$$1 \quad : \quad 0.436\ 83$$
Sodium oxide = 0.96 per cent.
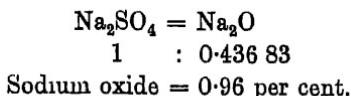
Sulphuric Anhydride.—100 c.cs. were acidulated with hydrochloric acid, the solution boiled, and the sulphuric anhydride precipitated as $BaSO_4$.

$$BaSO_4 = SO_3$$
$$1 \quad : \quad 0.342\ 93$$

Sulphuric anhydride = 0·96 per cent.
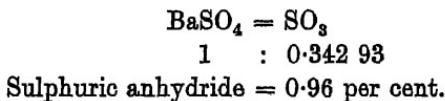
A " blank " determination of the sodium in the calcium carbonate used showed a deduction of 0·20 per cent. sodium to be necessary.

<center>*Result of Cryolite Analysis.*</center>

Sodium	.	.	.	.	.	31·66 per cent.
Aluminium	.	.	.	.	.	12·54 ,,
Fluorine	.	.	.	.	.	50·36 ,,
Sodium sulphate	.	.	.	.	2·19 ,,
Ferric oxide	.	.	.	.	.	0·20 ,,
Magnesia	.	.	.	.	.	0·19 ,,
Water	.	.	.	.	.	2·99 ,,
Zinc sulphide	.	.	.	.	0·19 ,,
Silica	.	.	.	.	.	0·06 ,,
Copper	.	.	.	.	.	Trace ,,

<center>100·38 per cent.</center>

5. Furnace Flux.

For commercial purposes an exhaustive analysis is very seldom required, if at all. The principal ingredients to be determined are : aluminium as metal, as alumina, and as cryolite, silica, and iron. The following are the results of two specimens. The aluminium carbide was most probably much higher in the fresh samples, but had decomposed before the analysis was proceeded with.

	(1)	(2)	
Metallic aluminium . .	2·10	0·76	per cen
Sodium fluoride . . .	4·61	7·61	,,
Ferric oxide . . .	0·91	0·67	,,
Alumina	28·72	17·10	,,
Carbon	3·69	1·67	..
Carbon dioxide . . .	Nil	0·44	,,
Sodium	19·07	Na_3AlF_6 22·94	,,
Aluminium . . .	7·47	$= 58·05$ 8·97	,,
Fluorine	31·51	per cent.37·70	,,
Lime	0·75	0·57	,,
Silica	1·26	1·66	,,
Aluminium carbide . .	0·12	0·03	,,
	100·21	100·12	,,

METHOD.

Sodium Fluoride.—A known weight, 2 to 5 gms,
agitated with cold water, filtered, and washed well T
filtrate is made up to a known volume, an aliquot porti
taken, and evaporated to dryness, with slight excess
sulphuric acid. Ignite, cool, and weigh the sodium sulpha
the operation being done in a platinum basin.

$$Na_2SO_4 = 2Na$$
$$1 \quad : \quad 0·324\,28$$
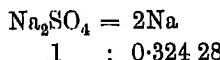
To another portion of the soluble in water, in a porcel
basin, add an excess of calcium chloride solution, and b
Allow the precipitate to subside, washing it twice by dec
tation, then transfer the precipitate to a filter paper a
wash free from soluble salts with hot water, dry in a ste
oven, ignite at a red heat, cool, and weigh the calc
fluoride, CaF_2 Calculate per cent. of fluorine.

$$CaF_2 = F_2.$$
$$1 : 0·486\,7.$$
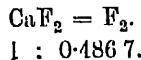
If this is found to be equivalent to the sodium found in the portion soluble in water, then evidently it must exist as sodium fluoride, NaF.

Carbon dioxide, as carbonate, may be determined as follows by the aid of a Schrotter apparatus (fig. 12) :—

A is a flask in which the decomposition of the sample is effected ; communicating with this flask there are two reservoirs, B and C, also a stoppered opening, D, which serves for introducing the sample. The reservoir B is filled with
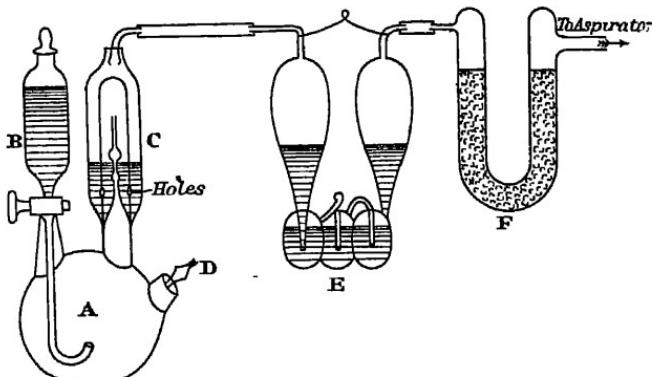
Fig. 12.—Schrotter Apparatus.

1 : 4 sulphuric acid ; the reservoir C is half filled with strong sulphuric acid. Ten gms. of the sample are weighed and transferred to the flask A, and the whole apparatus connected to the weighed bulbs E, containing caustic potash solution (33 per cent), which in turn are connected to the " U " tube F, containing lumps of calcium chloride The dilute acid in B is slowly run into A by removing the stopper and gradually turning the stopcock and regulating the aspirator, which is connected to the calcium chloride tube F, very carefully When all the acid from B has been run into A, a potash bulb similar to E is connected to the unstoppered neck of the reservoir B, to retain the carbon dioxide present in the

air and prevent it being absorbed by the potash bulbs E.
The speed of the bubbles of gas through the potash bulbs
should never be faster than can be counted.

Besides carbon dioxide there may be evolved hydrogen
and methane by the action of the acid on metallic aluminium
and the water on aluminium carbide respectively. However,
as these are not absorbed by either sulphuric acid or caustic
potash solutions, they will just pass through the whole
apparatus. It is also advisable to have some clear solution
of calcium sulphate in the flask A during the operation,
to retain any small amounts of hydrofluoric acid that may
be disengaged. After all action has ceased, continue aspirat-
ing for about one hour so as to ensure all the carbon dioxide
being carried over and absorbed by the potash, and any
hydrogen and methane displaced from the apparatus. The
potash bulbs E are then disconnected and weighed, the in-
crease being due to the absorption of carbon dioxide, CO_2.

The total sodium and fluorine are determined exactly as
in cryolite. The sodium and fluorine existing as sodium
fluoride is determined in the soluble-in-water portion and
deducted from the total sodium and fluorine. The remaining
sodium and fluorine are calculated to cryolite, Na_3AlF_6, its
equivalent of aluminium calculated, which is subsequently
deducted from the total aluminium.

$$Na_3AlF_6$$
$$\underbrace{69 : 27 \cdot 02 : 114}_{210 \cdot 02}$$
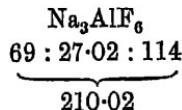
Therefore, if x equals percentage Na as cryolite, then

$$\frac{x. \, 27 \cdot 02}{69} = \text{per cent. Al} = \text{to } x \text{ per cent.}$$

or if $Y = $ per cent. fluorine as cryolite,

then $\dfrac{Y \, 27 \cdot 02}{114} = \text{per cent. Al} = \text{to } Y \text{ per cent.}$

Determination of Total Aluminium, Lime, and Ferric Oxide —Two gms. are treated in a platinum basin with pure caustic soda solution until all metallic aluminium is attacked, then carefully dry, and fuse with potassium bisulphate, proceeding as with cryolite.

The silica is also determined in the same way as in cryolite.

Burette
Funnel
Lead Pipe
(open end
Sample tipped out
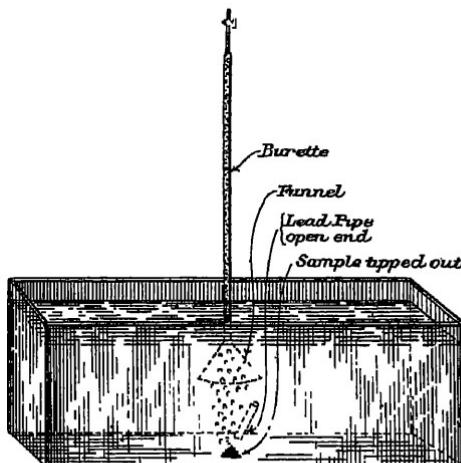
FIG. 13.—Methane Collecting Apparatus.

The residue in the platinum still may also be used for a check iron determination.

Estimation of the Aluminium Carbide.—In contact with water this decomposes with the evolution of methane.

$$Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4$$
$$(108 + 36) \quad = \quad 22{\cdot}4 \times 3 \text{ litres at N.T.P.}$$
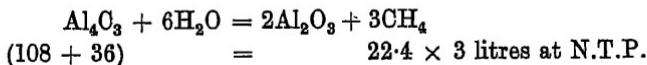
so that by measuring the volume of methane evolved its equivalent of aluminium carbide can be determined. Determination :—

Weigh 10 gms. of the furnace flux, and transfer to a

piece of lead tubing closed at one end; the open end is closed by means of the forefinger. It is thus transferred, in an inverted position, under the burette, which is filled with water as shown in fig. 13. The forefinger is then removed and the sample tipped out on to the bed of the trough, when the bubbles of methane will be seen to ascend and collect in the burette, where its volume is read off, after lowering the burette into the trough, until the level of the water in both the burette and trough coincide.

If the volume of methane evolved be small, a correction for pressure, temperature, and the tension of aqueous vapour need hardly be taken into account for ordinary purposes; but if a more accurate result is required, or if there be more than a few c.cs. of gas evolved, then these corrections should be made.

The following is the usual well-known formula in use :—

$$V = \frac{(P - w) \times 273 \times v}{760 \, (273 + t)} = \frac{(P - w) \times v}{760 \, (1 + 0{\cdot}003 \, 665t)}$$

where v = the observed volume of the gas,

t = the observed temperature,

w = the tension of aqueous vapour in a volume of the moist gas under pressure P,

and V = its volume when reduced to normal temperature and pressure.

If x = volume of methane, CH_4 at N T.P. in cubic centimetres, its equivalent of aluminium carbide, Al_4C_3, will be :—

$$\frac{144x}{67\,200} = \frac{9x}{4\,200} = y \text{ gms. } Al_4C_3.$$

Total Carbon.—This is accomplished best by direct combustion, as follows :—

A convenient weighed quantity of the sample (the amount depending upon the carbon contents) is mixed with recently ignited litharge, which retains the fluorine.

Fig 14 —Combustion Apparatus.

Combustion Furnace
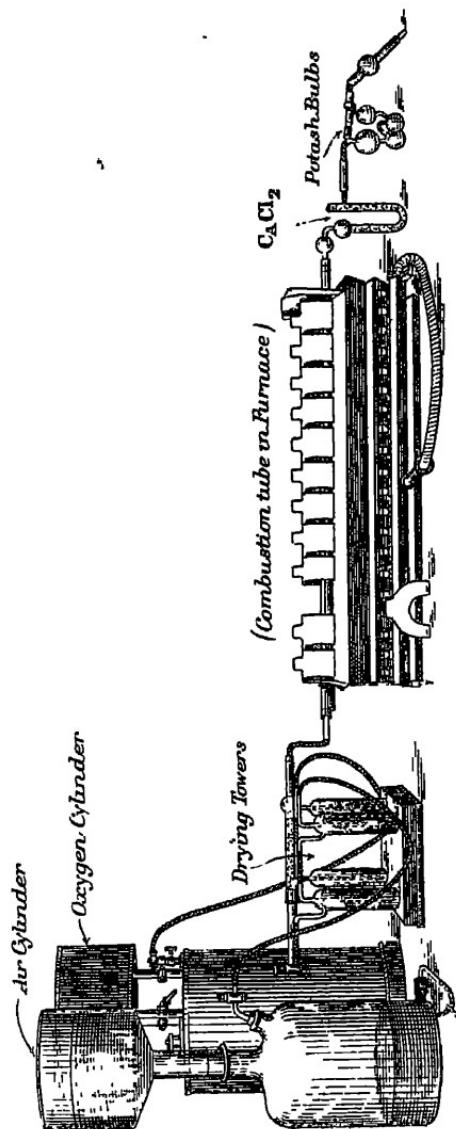
Fig 15.—Apparatus for determining Carbon by Combustion.

(Combustion tube in Furnace)

CaCl$_2$

Potash Bulbs

Air Cylinder

Oxygen Cylinder

Drying Towers

This mixture in a porcelain boat is burnt in the apparatus at e, fig. 14.

The combustion tube contains a glass plug d to prevent any backward diffusion ; e is the porcelain boat containing the sample mixed with the litharge ; f is granular copper oxide prepared by roasting short lengths of copper wire in a current of air.

Oxide prepared by igniting copper nitrate is very unsuitable for the purpose as it often evolves oxides of nitrogen when heated. g is a silver coil made by tightly coiling the metal gauze or sheet. h is a tube containing granular calcium chloride, through which CO_2 has been passed previously, if necessary, until its solution is neutral to test-paper, and the excess of CO_2 thoroughly removed by passing air through the " U " tube before connecting up to the apparatus (fig. 14). i is a " Geissler " bulb apparatus containing 33 per cent. potassium hydrate solution, with a calcium chloride tube (c) attached. A second larger calcium chloride tube j is attached to the small tube in order to prevent its contents from absorbing moisture from the atmosphere.

Everything is connected up, without the boat e containing the sample mixed with litharge, and the copper oxide f and metallic foil g heated to redness for at least half an hour, with a current of purified air passing through it in order to remove all combustible matter.

The bulbs i with the calcium chloride tube c are weighed, the boat e containing the sample to be burnt, mixed with litharge, placed in position, the whole apparatus connected up and made air-tight. The copper oxide f is now heated to redness, being careful not to heat the boat e. Start a slow current of oxygen through the tube, allowing the bubbles to pass at such a rate that they can be easily counted, then extend the heating to the boat e very gradually. The combustion should be complete and all the CO_2 absorbed

by the potash bulbs in forty-five minutes   The oxygen is now displaced by passing a current of purified air through the apparatus for about twenty minutes, after which the potash bulbs i, with the calcium chloride tube c, is detached and its contents immediately shut off from contact with the atmosphere.   After allowing to stand for half an hour near the balance-case to cool, it is weighed.   The increase in weight will be due to absorption of carbon dioxide, CO_2. After deducting the CO_2 found as carbonate in the determination as described on p. 71, the remaining CO_2 is calculated to carbon.

$$CO_2 = \quad\quad C$$
$$1 \quad : \quad 0 \cdot 27\,273.$$
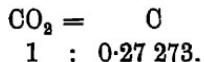
From this the carbon, existing as carbide (see p. 73), is deducted.

$$CH_4 = C$$
$$22\,400 \text{ c.cs.} = 12 \text{ gms.}$$
or
$$1 \text{ gm.} = 0\,75 \text{ gm.}$$
$$Al_4C_3 = 3C$$
$$1 \; : \; 0 \cdot 25$$
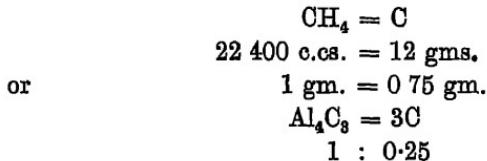
Then, after deducting the carbon in combination, the remainder is reported as free carbon.

Metallic Aluminium.—If this occurs in any quantity—such as large pieces—the simplest plan is to sieve it and test its purity ; but if present in small globules, and fairly well distributed throughout the sample, then the most practical method of determining the metallic aluminium is based upon the fact that when dissolved in caustic potash or soda, its equivalent of hydrogen gas is evolved.

Proceed as follows :—A convenient weighed quantity is first of all boiled with water to decompose the carbide, and filtered.   The insoluble on the filter, together with the paper, are dropped into a flask containing a solution of 40 per cent. caustic soda or potash (fig. 16).   A cork (india-rubber

stopper) with a delivery tube is immediately clamped into
the neck of the flask, and the evolved gas collected in a
measuring cylinder over water, as in the case of the deter-
mination of carbide (p. 73).

The delivery tube must extend fairly 'high up into the
collecting vessel, so that the gas (which will consist of air
and hydrogen) in the measuring cylinder is in communication
with that of the decomposing flask throughout the whole
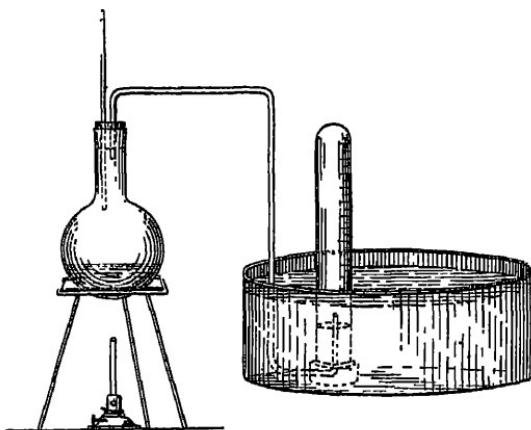
Fig. 16.—Hydrogen Collecting Apparatus

time, otherwise some water may be drawn back by suction,
due to the evolution of gas ceasing, and cooling of the
apparatus. A very gentle heating is usually required to
commence the reaction, and again towards the end of the
reaction, as the evolution of hydrogen ceases. The whole
apparatus is then allowed to cool, care being taken that the
gas in the collecting cylinder and that in the decomposition
flask are in direct communication throughout the whole
time, so that no water is sucked into the delivery tube,
which would otherwise alter the volume of gas

The volume of air and hydrogen which will be equal to

the volume of hydrogen evolved is measured and reduced to N.T.P. (normal temperature and pressure) in the same way as that of methane (p. 74).

From the equation

$$2Al + 6NaOH = 2Na_3AlO_3 + 3H_2$$
$$54 \text{ gms.} \qquad = 67\ 200 \text{ c.cs. at N.T.P.}$$
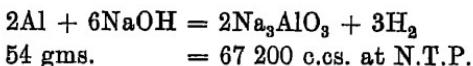
it will be seen that the volume of hydrogen evolved (A c.cs.) at N.T.P. will equal

$\dfrac{A \times 54}{67\ 200} =$ gms. of metallic aluminium in the weight of sample taken.

The metallic aluminium, the aluminium equal to the sodium and fluorine in the cryolite, and that existing as carbide are all deducted from the total aluminium, and the remainder is then calculated to alumina.

$$2Al = Al_2O_3$$
$$1\ :\ 1{\cdot}889$$
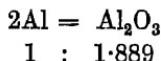
6. Oil Coke, Pitch, and Carbon Electrodes.

The crude oil coke contains a little moisture and some oil that has not been completely driven off in its manufacture. For the purpose of electrode manufacture the ash should be as low as possible, usually varying from 0·1 per cent. in the large lumps to 0·3 per cent in the small pieces. After calcining, the percentage of ash is increased owing to loss of carbon by burning. The sample of oil coke or carbon electrode is passed through a 40-mesh sieve for analysis

Moisture —Heat 10 gms. in a weighing bottle at 120–130° C for one hour, insert stopper, which must be a good-fitting one, cool, and weigh. Loss or decrease in weight report as moisture.

Volatile Matter.—Since there is great difficulty in driving off the volatile matter by means of heat without some slight

combustion taking place, the following method has been found to give the most uniform results :—

Weigh 2 gms. of the sample into a platinum crucible with a lid on, and heat for seven minutes over an ordinary flame 7 inches long   Cool, and weigh rapidly.   The loss in weight, minus the moisture, equals volatile matter.

Ash.—2 gms. of the finely ground material, in a platinum capsule, are heated for five to six hours at a dull red heat, and then at a red heat for fifteen minutes.   From time to time it is stirred with a platinum rod until all is burnt to ash.   Weigh, and calculate percentage of ash.   The ash usually consists of silica, ferric oxide, alumina, and sodium carbonate, which may be determined as follows :—

A portion of the ash is fused with about ten times its weight of sodium carbonate, extracted with dilute sulphuric acid, and then evaporated to fuming ;   cool, dilute with water, and filter off the silica, which is washed, dried, ignited, and weighed, etc.   The filtrate is made up to 250 c.cs.   Two portions of 100 c.cs. of this solution are measured off.

Iron.—In one portion the iron is determined by saturating with sulphuretted hydrogen, boiling off the excess of gas, taking care to exclude air from the flask.   Cool, and titrate with potassium permanganate solution (1 c.c. = $0 \cdot 002$ Fe_2O_3) in the same way as for iron in bauxite (p. 55).

Alumina.—To the other 100-c.c. portion add some ammonium chloride and slight excess of ammonia, boil for half a minute, and allow to stand in a warm place for half an hour.   Filter off the aluminium hydrate, ignite, and weigh as alumina, Al_2O_3.

Alkalies.—The alkalies are determined on a separate portion of the original ash, which is boiled with water and filtered. The filtrate is concentrated to a low bulk, made slightly alkaline with ammonia, and allowed to stand as for the alumina determination, and filtered.   The filtrate is acidified slightly with sulphuric acid, and the solution evaporated

to fuming in a platinum basin.   It is then heated at a dull
red heat until all the excess of sulphuric acid and ammonium
salts are driven off.   Cool, and weigh as Na_2SO_4, which is
usually calculated to the carbonate Na_2CO_3.

$$Na_2SO_4 = Na_2CO_3$$
$$1 \quad : \quad 0.7464$$
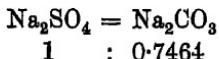
The potash occurs in such small quantities as a rule, that
for practical purposes it may be taken as sodium.

Density.—This may be determined in exactly the same
way as that of alumina (p. 61).

Porosity.—This may be calculated from the true and
apparent densities.   The apparent density is the weight of
1 c.c. of the material;   call this b.   The true density is
the weight divided by the volume actually occupied by the
material;   call this a

The value of a may be determined by " Zellner's method,"
which consists of mixing bromoform and chloroform in such
proportions that small pieces of the carbon, the density of
which is being determined, will neither sink nor float when
saturated with the mixture.   The fluid mixture will then
be of the same density as the piece of carbon.   The density
of the mixture of bromoform and chloroform is determined
by any of the well-known methods.   This will give the value
of a, and the value of the porosity will be

$$100\,\frac{a - b}{a} = \text{porosity per cent}$$

Analysis of Pitch—The pitch used in the manufacture of
carbon electrodes is generally so free from inorganic material
that the ash is practically nil, the density and volatile matter
generally being the only determinations that will be found
necessary.   The volatile matter is usually about 64 per cent.,
and is determined in the same way as that in coal;   that is
to say, 2 gms. of the pitch in a platinum crucible with lid

6

on is placed in a red-hot muffle gas furnace until the flame issuing from between the crucible and lid just dies out, when it is immediately removed to a cool place and weighed as soon as cold.   Loss equals volatile matter.

Density.—For this purpose obtain a wide-mouthed weighing bottle of about 50 c cs. capacity, having a good-fitting stopper. With a file scratch a groove down the side of this stopper. The weighed bottle is filled with water of a temperature above that of the melting-point of the pitch the density of which is to be determined.   The stopper which should also be weighed with the weighing bottle at each weighing, is inserted in the neck of the bottle, and any excess of water squeezed out by the groove in the lid or stopper.   The outside is carefully dried, cooled, and weighed.   Weight of bottle, stopper, and water, minus the weight of bottle and stopper, will give the number of gms. of water required to fill the bottle at the temperature at which it was filled.   Call this weight of gms A c c

The vessel is now very carefully emptied, dried both inside and out, and filled in exactly the same way as with water, only this time with the pitch, which has been previously melted and heated to the same temperature as that of the water.   The stopper is inserted, and the excess of pitch squeezed out.   Cool, and weigh.   This weight, minus the weight of the bottle and stopper, call B gms.   Then weight of B will be equal to volume A.

Therefore, at temperature T, $\dfrac{B}{A} =$ density of pitch at temperature T.

An approximate calculation of mixtures of coke and pitch may be made if the volatile matter in the coke, pitch, and the mixture be known.

$$\text{Let } x = \text{pitch in 100 parts}$$
$$\text{then } (1 - x) = \text{oil coke in 100 parts}$$
$$\text{then} \qquad \frac{yx + b(1 - x)}{100} = z.$$

Where y = per cent. of volatile matter in the pitch,

„ b = per cent. of volatile matter in the coke,

and z = per cent of volatile matter in the mixture.

Example.—A mixture of coke having 1·03 per cent. volatile matter, and pitch having 60·0 per cent. volatile matter, had 12·5 per cent. of volatile matter.

$$\therefore \quad \frac{60x + 1\cdot03\,(1 - x)}{100} = 12\cdot5$$

$$\therefore \quad 60x + 1\cdot03 - 1\cdot03x = 12\cdot5 \times 100$$

$$\therefore \quad 58\cdot97x = 1\,250 - 1\cdot03$$

$$\therefore \quad x = \frac{124\,897}{5\,897} = 21 \text{ approximately.}$$

Therefore approximate per cent of pitch in the mixture = 21 per cent.

7. Producer Gas and Coal.

The coal used for the generation of producer gas, for use in the calcining of the carbon electrodes, is usually of a very inferior quality. If anthracite, the ash often amounts to over 15 per cent. The volatile matter is determined in the same way as in pitch (p. 79), after which the coke is tipped out on to a capsule and burnt to ash at a red heat.

The total sulphur may be determined as follows ·—Weigh off 1 gm. of the finely ground coal, and mix with four times its weight of pure lime, slake with water, and dry in the steam oven at 100° C. Then ignite and burn to ash, and cool. The mass is then covered with 15 to 20 c.cs. of bromine water, rinsed with water into a beaker, and acidified with hydrochloric acid, boiled and filtered, and the sulphate in the filtrate precipitated by adding an excess of barium chloride. The barium sulphate is filtered off, washed free from chlorides, dried, ignited, and weighed as $BaSO_4$.

$$BaSO_4 = S$$
$$1 \quad : \quad 0\cdot137\,32$$
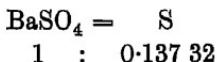
Calorific Power.—This is determined by ascertaining the number of heat units which are evolved by the combustion of unit weight of the fuel in oxygen. One heat unit, or " calorie," is the amount of heat which is required to raise the temperature of 1 gm. of water 1 degree centigrade.

The calorific power of coal may be estimated by the Lewis Thompson calorimeter, using a mixture of potassium nitrate and potassium chlorate to supply the oxygen. The results
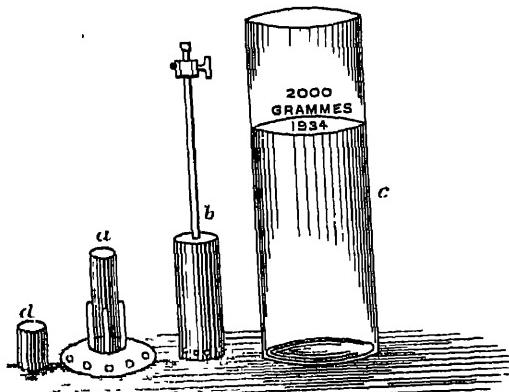
FIG. 17.—Lewis Thompson Calorimeter.

furnished by this apparatus are only approximately accurate, but they suffice for the commercial valuation of the heating power of coal.

The Lewis Thompson calorimeter is shown in fig. 17. *c* is a glass cylinder which holds 2 000 gms. of water when it is filled up to the etched mark, and a suitable metal vessel and tube in which the fuel can be burnt. When the calorimeter is to be used, fill it to the mark with water at a temperature of about 15·5° C.

Weigh out accurately 2 gms. of the finely powdered sifted coal. Mix this intimately with ten times its weight of a

mixture of one part of potassium nitrate and three parts of potassium chlorate, which has been previously well dried in the steam oven, and transfer to the copper tube (*a*) seen on the left hand in the figure, and gently tap the tube on the bench so as to cause the mass to settle down. The broader tube (*d*) is intended for a mixture which does not burn readily. Now bury into the upper part of the powder the lower end of piece of fuse, which is made by steeping thin cotton wick in nitre solution and drying it.

Place the tube in the brass clips attached to the brass disc, and proceed to render the temperature of the water in the calorimeter uniform by stirring, the temperature being carefully taken by means of a delicate thermometer. Now light the fuse, rapidly push on the cover *b*, taking care that the stopcock is closed, and immerse the tube in the water until it stands upon the bottom of the cylinder. The mixture will burn, and the gaseous products of combustion will force their way through the holes at the base of the copper cylinder, and will pass up through the water into the air.

After the combustion has ceased, the stopcock is opened so as to admit water to the interior of the metal apparatus. The metal apparatus is alternately raised and lowered several times so as to mix the water thoroughly, and the temperature of the water is once more taken carefully by a delicate thermometer. The number of centigrade degrees by which the water has increased in temperature during the combustion is added to the number of degrees corresponding to the amount of heat absorbed by the apparatus ; the latter may be taken as being one-tenth of the rise of temperature observed, and since 2 gms. of coal were used, and the glass cylinder contained 2 000 gms. of water, this number of degrees, when multiplied by 1 000, will give the number of heat units, or calories, evolved by unit weight of the coal.

As an example in a particular estimation, the initial tem-

perature of the water was 17° C., and the final temperature of the water was 23·9° C. Assuming that the heat absorbed by the apparatus measured one-tenth of the observed rise in temperature of the water, the calorific power will be equal to $(6·9 \times 0·69) \times 1\,000 = 7\,590$ calories or heat units

A second graduation will be seen on the glass cylinder at 1 931 c.cs. The cylinder may be filled with water up to this mark, and the temperatures taken in Fahrenheit degrees. The number of degrees rise in temperature registered on the thermometer after the combustion, if increased by one-tenth of their amount, will then represent the number of pounds of water which the burning of one pound of the coal will convert into steam.

The calculation is based on the assumption that $\dfrac{1\,934}{2} = 967$ Fahrenheit units of heat are required to convert the unit weight of water into steam.

In a gas producer where steam is admitted, it is reduced to the monoxide of carbon and hydrogen, the oxygen ir this case not being mixed with incombustible nitrogen as i the case when air is used in the place of steam. But as the same amount of heat is absorbed in the reduction o the steam (water) as is given out again in its production o combination, heat will be absorbed. Hence the quantity of steam admissible is limited.

To decompose nine parts of water 34 462 calories are re quired. Eight parts by weight of oxygen, combining witl six parts of carbon to form CO, gives out $2\,473 \times 6 = 14\,83$ calories.

$$\therefore \quad 34\,462 - 14\,838 = 19\,624 \text{ calories lost.}$$

In practice it is found that the best results are obtaine by using 5 per cent. of steam.

The quantity of hydrogen converted into methane is pract cally nil, but sulphuretted hydrogen is sometimes formed.

Producer Gas.—This is most readily analysed by sub-jecting a known volume to absorption by different solutions.

An "Orsat" gas apparatus (fig. 18) will be found convenient. Although there are a large variety of designs of gas apparatus
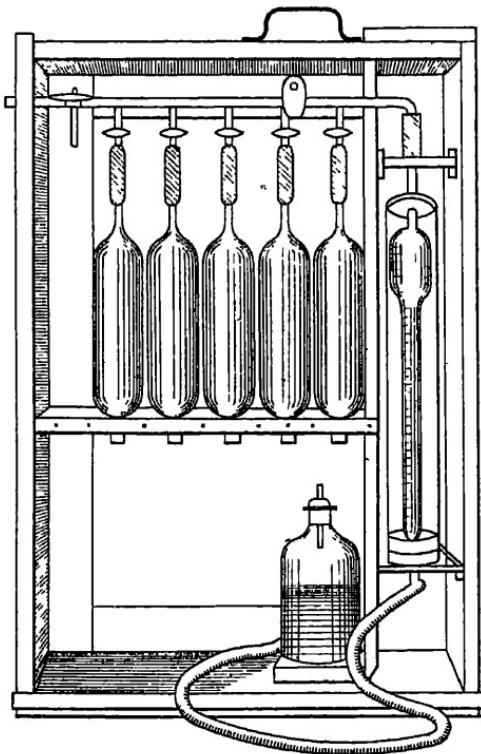
`Fig. 18.—"Orsat" Gas Apparatus.

to choose from, the principle in every case is the same. The gas is passed over, back and forward, each of the following solutions until no further contraction in volume takes place. The volume of the contraction corresponds to that of the gas that has been absorbed. Proceed in the follow-ing order :—

1. Carbon dioxide. This is the first gas to be extracted which is absorbed by the potassium hydrate solution (a).

2. The olefines are next absorbed by water saturated with bromine, and subsequent removal of the bromine vapour by means of the potassium hydrate solution.

3. Benzene is now removed by passing the gas over fuming nitric acid, and the subsequent removal of the nitrogen oxides by means of the potassium hydrate solution.

4. Oxygen—absorbed by means of the alkaline pyrogallate solution (b).

5. Carbon monoxide is then absorbed by freshly made cuprous chloride dissolved in hydrochloric acid (Solution c.)

6. The residual gas may consist of hydrogen, nitrogen, and perhaps a little methane. The hydrogen may be determined by combustion over the palladinised asbestos tube usually supplied with the gas apparatus. The gas is passed back and forward through the warm tube until no more contraction takes place. Or the hydrogen and methane may be mixed with oxygen and fired simultaneously. In either case the nitrogen is measured by difference. For the latter method about 30 c.cs. of the mixture of hydrogen, methane, and nitrogen is made up to 75 c.cs. with oxygen, and the mixture fired from an induction coil in a special form of absorption bulb supplied with the apparatus for the purpose. The contraction is noted, then the further contraction after absorption with caustic potash solution.

Then if $x =$ contraction of volume caused by firing, and $y =$ contraction of volume caused by absorption of the caustic soda, or potash solution, then the volume of hydrogen in the volume of mixed gases $= \frac{2}{3}(x - 2y)$, and the volume of methane will be that of y ; that is, the same volume as that of the carbon dioxide (CO_2) absorbed.

The solutions required for the above absorptions are made up as follows :—

(*a*) Dissolve 320 gms. of potassium hydrate sticks in 130 c.cs. of water = about 400 c.cs. altogether.

(*b*) Dissolve 10 gms. of pyrogallic acid in 200 c.cs of the above potash solution (*a*).

(*c*) Dissolve 27 gms. of cuprous chloride in 200 c.cs. of hydrochloric acid of 1·124 specific gravity. This will absorb about 10 c.cs. of CO.

8. Metallic Aluminium.

The commercial metal contains as impurities, silicon, iron, and small amounts of sodium, and very minute amounts of carbon, oxygen, and nitrogen. The silicon, as a rule, varies from 0·10 per cent. to 0·70 per cent., the iron from 0·15 per cent. to 0 80 per cent., and the sodium from 0·002 per cent. to 0·04 per cent. At present no satisfactory accurate methods of determining the small amounts of nitrogen, oxygen, and carbon present in metallic aluminium have been attained, so that these are never determined except for special scientific investigations.

Silicon.—This occurs in at least three forms, viz.: (1) as silicide of aluminium or possibly as silicide of iron ; (2) as graphitic silicon ; (3) as silica.

Kohn-Abrest has investigated the effect of heating metallic aluminium in a porcelain tube to 1 100° C. in a vacuum. At first the metal volatilises readily, but after some time no further sublimation takes place. It is shown that a silicide of aluminium (Al_2Si) is produced, which on mixing with the metal appears to raise its boiling-point.

The same effect is produced if the aluminium is isolated from the porcelain tube in a boat of graphite, which would seem to indicate that in one form or another the silicon must have passed through a vapour phase.

As the effect of the different forms of silicon in aluminium are at the present time not much known, therefore only

the total silicon is usually determined for commer
purposes.

For the estimation, to 1 gm. of the metal turning
a 400-c.c. beaker add 20 c.cs. water, 5 c.cs. concentra
nitric acid, 5 c.cs concentrated sulphuric acid, together w
just sufficient hydrochloric acid to effect solution. The lat
is added from time to time in small amounts, the tc
quantity seldom exceeding 10 c.cs.

When solution is complete, it is evaporated to dryr
until dense white fumes are evolved. During this stage
is advisable to keep the beaker covered with a watch
clock glass to prevent any loss by spirting.

When cooled, dilute to about 200 c.cs. with warm wa
bring to the boil, and allow it to stand in a warm pl
until all the silky-looking aluminium sulphate has dissol
completely. This usually takes about ten minutes Ii
is doubtful whether all the sulphates have dissolved
little hydrochloric acid may be added, but is seldom necessa
The insoluble is then filtered off (preferably through a
Schleicher and Schull, No. 589, black-band filter paper, wh
has been found to answer the purpose best). The I
cipitate is washed free from sulphates with hot water, igni
until the weight remains constant.

This insoluble, for commercial purposes, may be assur
to consist of only silica, although really most of the graph
silicon is not converted into oxide by this treatment,
oxidation only taking place on the surface. For a m
accurate determination this mixture of silicon and si
may be fused with fusion mixture, and the melt extrac
with dilute hydrochloric acid, the solution evaporated
dryness, baked, moistened with hydrochloric acid, dilu
with hot water, boiled, filtered, and the total silicon
silica weighed. Calculate percentage of Si.

$$SiO_2 = Si$$
$$1 \quad : \quad 0.46\,703$$
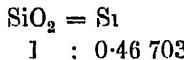
To determine the silicon existing in the graphitic state and that in the combined state, proceed as in the first methoc (p. 90), omitting the nitric acid, and dissolving in a flasl instead of a beaker.   The gases and vapour from this flasl are passed through two " U " tubes containing bromine water, and then through a " U " tube containing ammonia water, to retain any silicon hydride (SiH_4) that may be evolved, which are recovered by mixing these solutions boiling off the bromine, and then adding the solution to tha contained in the flask.   The whole solution will now contain the graphitic silicon as Si, and the combined silicon as silicic acid   The solution is then evaporated, fumed, diluted witl hot water, filtered, ignited for a short while, and weighed Call this weight A.

The graphitic and combined silicon (weight A) is nov fused with fusion mixture, and the total silicon determinec as on p. 90.   The result A minus the total silicon will give the amount of oxygen equal to the combined silicon.

$$O_2 = Si$$
$$32 \; : \; 28$$

and the combined silicon deducted from that of the tota silicon will give the amount of graphitic silicon.

Iron.—For the determination of iron the " Regelsberger ' method, modified as follows, gives quick and accurat results.

One gm. of medium-sized turnings is placed in a 40C c c. conical flask having a small funnel in the neck to ac as a valve   A piece of pure caustic soda solution, abou 7 or 8 gms. (about one-third of a stick) is added, and 2 to 30 c.cs. warm water run in by the funnel   A vigorou action ensues, during which time some 25 per cent. su phuric acid (approximately 25 per cent. to 30 per cent.) made up, and as soon as solution of the metal in the caust soda is complete, the warm sulphuric acid solution is run i

by the funnel until a clear solution in excess of the acid
is obtained.   The flask is rapidly cooled and titrated with
standard potassium permanganate until a slight permanent
pink colour is produced.   The standard permanganate
solution should be of such a strength that 1 c.c. will equal
0·001 gm. Fe.

Sodium.—The following method is practically the only
satisfactory one, and is based on the fact that aluminium
nitrate is decomposed at a temperature of 250° C., giving
insoluble alumina.

From 3 to 5 gms. of the metallic turnings are placed
in a covered porcelain dish, 50 c.cs. strong nitric acid are
added.   Small amounts at a time of hydrochloric acid are
added to assist solution.   When solution is complete, it is
evaporated to dryness and the residue heated strongly over
an Argand burner, the pieces being broken up by means of
a rod.   Cool, and again moisten with concentrated nitric
acid, and again take to dryness, this time breaking the
residue up with a glass rod until all of it is reduced to powder,
and no brown fumes are evolved on crushing.   The mass
is then extracted with hot water containing a little am-
monium carbonate, and ammonia, and filtered.   The filtrate is
evaporated to dryness, taken up with water, a little ammonium
carbonate and ammonia added, and filtered into a weighed
platinum basin, converted into either chloride or sulphate
and weighed as such, as described for bauxite (pp. 48, 57).

9. Aluminium Alloys.

The common alloys that are met with are those of copper,
zinc, and nickel.   Sometimes lead occurs as an impurity
in the zinc alloys, but only in small amounts.   The rarer alloys
are those of manganese, titanium, tungsten, and magnesium.

Copper.—For alloys rich in copper, such as aluminium
bronze, with 90 per cent. Cu, no special method is necessary,

as it can be treated by any of the usual methods, such as dissolving in nitric acid, neutralising with sodium carbonate, adding a slight excess, and then made acid with acetic acid, an excess of potassium iodide added, and the liberated iodine titrated with a standard solution of " hypo " (1 c.c. $= 0 \cdot 01$ gm. Cu), using a little starch as indicator, which strikes a blue colour with iodine. The strength of the " hypo " solution (sodium thiosulphate, $Na_2S_2O_3,5H_2O$, dissolved in water) is determined by weighing some copper foil, dissolving in nitric acid, and proceeding in the same way as the copper alloy.

For alloys containing up to, say, 6 or 7 per cent. it is found best to separate the copper from the filtrate obtained from the silicon and silica determination by precipitation with sulphuretted hydrogen, and the copper sulphide filtered off, dissolved in nitric acid, neutralised with sodium carbonate, acidified with acetic acid, excess of potassium iodide added, and titrated with standard sodium thiosulphate solution, and the copper estimated as before.

Zinc, nickel, and copper may be determined in the same portion of sample by " Seligman and Willott's " method, which is as follows :—

0·5 gm. or 1 gm. of the metallic turnings are dissolved in caustic soda in the same way as for the iron determination in metallic aluminium (p. 91). The contents are then diluted to about 300 c.cs. and filtered. The insoluble may consist of nickel, iron, and copper, which is dissolved in hydrochloric acid and a few drops of nitric acid, and the copper removed by means of sulphuretted hydrogen. This is filtered off and determined by solution in nitric acid, made ammoniacal, and the colour compared in a Nessler tube with a similar solution of known copper contents The main filtrate from the sulphide precipitate is boiled till free from sulphuretted hydrogen, and the solution diluted to about 200 c.cs. with hot water, any iron removed by a slight excess

of ammonia, and the nickel in the filtrate precipitated by
adding an excess of caustic soda, and a few drops of bromine
water added, boiled, filtered off, and redissolved in acid,
and again precipitated with caustic soda and a few drops
of bromine, ignited, and weighed.

$$NiO = Ni$$
$$1 \quad : \quad 0{\cdot}781\ 94$$
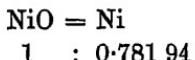
The combined filtrates from the nickel and copper are
added to the main filtrate from the sample dissolved in
caustic soda.

The zinc in this filtrate is separated by gassing with
sulphuretted hydrogen until a skin of aluminium hydrate
begins to form over the gas bubbles as they reach the surface
of the liquid   The zinc sulphide is filtered off and dissolved
in as little hydrochloric acid as possible, and 2 c.cs   of
concentrated hydrochloric acid added in excess, diluted to
about 200 c.cs   (If tin be present it must be removed by
sulphuretted hydrogen at this point.)   The zinc is then
titrated with standard ferro-cyanide solution.   The solution
of zinc is kept nearly on the boil during the titration.   A
slight excess of ferro-cyanide strikes a yellow-ochre colour
with a uranium salt, usually the acetate, drops of which are
placed on a white porcelain tile, while drops of the solution
being titrated, are added to the drops of uranium salt
solution until the yellow-ochre colour is permanent.   The
equivalent of zinc of the potassium ferro-cyanide is found
by titrating with some pure zinc.

Aluminium.—In the pure metal or alloys rich in aluminium
this is nearly always taken by difference (100—impurities) as
no accurate method is known.   In the heavy alloy it is
usually separated as phosphate or hydrate thus : dissolve
in the same way as for silicon in aluminium (p. 90).   The
filtrate from the silicon is saturated with sulphuretted
hydrogen, filtered.   The filtrate is *nearly* neutralised with

dilute ammonium hydrate solution, a little sodium hyposulphite is added in order to reduce any iron, and then 2 to 3 c.cs. of a saturated solution of sodium phosphate. Finally add 5 or 6 gms. of sodium acetate dissolved in a little water. The solution is boiled until it no longer smells of sulphurous acid, and filter it. Wash, dry, ignite, and weigh the precipitate of aluminium phosphate, $AlPO_4$.

$$AlPO_4 = Al$$
$$1 \quad : \quad 0.221\ 8$$
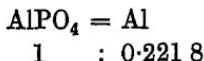
Lead.—This will have been obtained with the silica, and, when suspected, is determined by treating the insoluble silica, silicon, and lead sulphate with hydrofluoric acid and a few drops of sulphuric acid, to volatilise the silica   The residual lead sulphate is fused with sodium carbonate, extracted with water, and the insoluble dissolved in hot solution of hydrochloric acid, and the lead present precipitated by means of sulphuretted hydrogen, filtered, dissolved in a few drops of nitric acid, and converted into sulphate, and weighed as such

Magnesium.—2 gms are dissolved in hydrochloric acid, a little nitric acid added if necessary, and the copper removed in the usual way with sulphuretted hydrogen 15 gms. of tartaric acid are added, and the solution carefully just neutralised with ammonia, and 5 gms. of ammonium chloride added. Sulphuretted hydrogen is again passed to precipitate any Fe, Ni, Zn, and most of the manganese that may be present. After allowing to clot, the precipitate is filtered and washed with 2 per cent. AmCl solution. The solution is then boiled to drive off the sulphuretted hydrogen. The bulk of the solution should be made about 300 c.cs., and made slightly alkaline with ammonia   Five gms. of sodium hydrogen phosphate, Na_2HPO_4, dissolved in water, are now added slowly with vigorous stirring and allowed to stand overnight, after adding nearly half its bulk

of ammonia. Next morning the precipitate is filtered off
and redissolved in hydrochloric acid, and again precipitated
as before, after adding 1 gm. of tartaric acid. The second
precipitation is necessary, as a lot of tartrate usually crystal-
lises out in the first precipitation The magnesium phos-
phate is filtered off, washed free from soluble salts with
cold ammonia water, dried, ignited, and weighed as mag-
nesium pyro-phosphate.

$$Mg_2P_2O_7 = 2Mg$$
$$1 \quad : \quad 0\cdot218\ 75$$
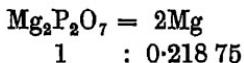
A quicker method, although not so accurate as the fore-
going, is to dissolve in hydrochloric acid and a little nitric
acid, separating the copper with sulphuretted hydrogen as
before.

The aluminium and iron are now precipitated as basic
acetates as follows :—

The excess of sulphuretted hydrogen is boiled off, and the
acid solution neutralised with ammonium carbonate very
carefully, until only a slight precipitate persists on stirring.
Now add a little acetic acid and a moderate quantity of
strong ammonium acetate solution, and boil for a short time.
The solution is transferred to a graduated flask (1 or 2 litres
capacity), cooled, and made up to a known volume, and
allowed to clear by standing, and the clear solution decanted
through a dry filter. Nitric acid is added to a measured
portion of the filtrate, which is boiled down to low bulk,
made ammoniacal, and the magnesium precipitated by
adding ammonium phosphate with constant stirring, about
one-third to half its bulk of strong ammonia solution added,
and allowed to stand a few hours before filtering, after which
it is dried and ignited, as before, as $Mg_2P_2O_7$.

Titanium.—This may be determined either by separating
with sulphurous acid, or colorimetrically in the filtrate from
the silica, as described for bauxite (pp. 44, 53).

Manganese.—The bismuthate method is very suitable for the rapid determination of manganese in aluminium alloys.

The method is as follows :—One gm. of the sample is dissolved in 50 c.cs. nitric acid. If difficulty is experienced in dissolving in nitric acid alone, then solution is effected by means of aqua regia, and the solution taken to dryness, with slight excess of sulphuric acid, to get rid of all hydrochloric acid, as the latter interferes with the determination. The mass is then taken up with 30 c cs. 1·20 nitric acid.

If soluble in concentrated nitric acid, any organic matter, possibly a little carbon, is oxidised by adding bismuthate (preparation of which, see below) and boiling, the solution is cooled and diluted to about 100 c.cs. ; 20 c cs. 1·20 nitric acid being added.

Whether the sample was dissolved in aqua regia or nitric acid alone, proceed from here as follows :—After adding the 1·2 sp. gr. nitric acid, an excess of bismuthate is added, and the solution shaken well, then filtered through asbestos. When the manganese is in quantity the filtrate is diluted to about 200 c.cs., an excess of standard ferrous sulphate added, and the excess titrated with decinormal permanganate solution ; but if the manganese be present in small quantity, the manganese may be estimated merely by comparison of the colour of the permanganate solution with that of a solution of known strength

Preparation of Sodium Bismuthate —Reddrop and Ramages give the following instructions in the preparation of this compound ·—

Heat twenty parts of caustic soda nearly to redness in an iron crucible, and add, in small quantities at a time, ten parts of basic bismuth nitrate, which has been dried in a water bath. Two parts of sodium peroxide are then added, and the brownish fused mass is poured out on to an iron plate to cool. When cold, it is broken up in a mortar, extracted with water, and collected on an asbestos filter.

7

The residue, after being washed four or five times by decantation, is dried in the water oven, then ground, and passed through a fine sieve. Its oxidising power is determined by adding half a gm. to a measured amount of ferrous sulphate or hydrogen peroxide, and titrating the excess with decinormal permanganate solution. 1 gm. of the bismuthate usually is equal to between 50 and 60 c.cs. of $\frac{N}{10}$ $K_2Mn_2O_8$.

Tungsten.—The sample is dissolved in just sufficient hydrochloric acid, and a little nitric acid, to decolourise any dark residue. The solution is then diluted to 200 c.cs., and an excess of sodium hydrate added, boiled, and filtered. The filtrate is poured, with constant stirring, into boiling hydrochloric acid ($3HCl : 1H_2O$) so that about 10 c.cs. of the acid is in excess of that required. The solution is now slowly evaporated to about 250 c.cs., and the precipitate of tungstic acid filtered off. The filtrate is again boiled some time and evaporated somewhat, any further precipitate of tungstic acid being then filtered off. The combined precipitates are then ignited and weighed as WO_3.

$$WO_3 = W$$
$$1 \quad : 0.793$$
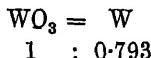
The above method requires some practice to obtain accurate results. I have obtained accurate results by treating the precipitate of silica obtained as described on p. 90, which will contain any tungsten that may be present, with hydrofluoric acid and a few drops of sulphuric acid to volatilise the silicon, then igniting strongly, and weighing the yellow tungsten oxide, WO_3.

In special cases, where it is desired to separate all the metals that may be present, they may be separated by means of the usual " group reagents," a detailed account of which appears in almost every text-book on qualitative analysis.

In proceeding with such an examination it is advisable to separate Si, $PbSO_4$, W, Ti, Au, and Pt, before adding the various group reagents, HCl, H_2S, AmOH, Am_2S, Am_2CO_3, etc. In such a case, dissolve the metal in aqua regia, and evaporate to fuming with slight excess of sulphuric acid, diluting with water, and boiling a short time, only until all the silky aluminium sulphate has passed into solution, then filter and examine precipitate according to Table (A).

TABLE (A).

Precipitate may contain—

Si, SiO_2, $PbSO_4$, WO_3 + some TiO_2.

Fuse with $KHSO_4$, extract with cold water.

Soluble.	Insoluble.
WO_3, $TiO_2 + H_2O_2$, and determine Ti by the yellow colour produced. Then evaporate to fuming with concentrated H_2SO_4 and determine WO_3.	SiO_2, $PbSO_4$. Volatilise SiO_2 with HF + H_2SO_4. Loss $= SiO_2$. Residue $= PbSO_4$.

The main solution is diluted until there is about $\frac{1}{2}$ per cent of sulphuric acid in excess, excess of SO_2 added, and the solution boiled some time, say, for one hour. Examine according to (B).

TABLE (B).

The precipitate may contain TiO_2, Au, and Pt. Dissolve in aqua regia, take to dryness with sulphuric acid, dilute, boil.

Precipitate $= TiO_2$, hydrated.	Solution may contain Au $+ Pt, +$ oxalic acid. Boil Au precipitated, filter, and add AmCl to filtrate. Concentrate filtrate, and precipitate Pt as $2NH_4Cl$, $PtCl_4$.

The main filtrate, from the sulphurous and sulphuric acid solution, is then boiled until free from sulphurous acid (SO_2). The solution is then treated with the usual " group reagents " for the separations of the metals.

TABLE OF PHYSICAL AND MECHANICAL PROPERTIES OF ALUMINIUM.

Atomic weight, 27·1.

Atomic volume $\left(\dfrac{\text{atomic weight}}{\text{specific gravity}}\right) = 10\cdot4$.

Atomic heat (specific heat $\times$ atomic weight) $= 6\cdot02$.

Specific gravity (cast), 2·6.

Melting-point, 657° C.

Specific heat, 0 167 at 15° C. and 0·308 near the freezing-point.

Specific volume, 0·384 6.

Density, lbs. per cubic foot, 161·7.

Coefficient of expansion of volume per degree Fahr., 0·000 034.

Coefficient of linear expansion (mean of 1° C. to 100° C.) $= 0\cdot000\,023$.

Coefficient of contraction, just below its freezing-point, about 1·6 per cent.

Tensile strength, about 17 tons per square inch.

Limit of elasticity, in lbs. per square inch cross-section = 19 376.

Breaking load, in lbs. per square inch cross-section = 28 200.

Order of malleability, between silver and copper.

Order of ductility, between platinum and iron.

Hardness, according to " Moh's " classification = 2.

Specific electrical resistance in 10^{-6} legal ohms at 15° C., 2·762.

Electrical conductivity per cent. in terms of Mathiessen's standard taken to be

$$1·696 \times 10^{-6} \text{ legal ohms at 15° C. for copper} = 61·5.$$

Average temperature coefficient per 1° C. between 0° C. and 100° C., 0 003 93.

Yield per ampere hour = 0·336 8 gm. Al.

INDEX.

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